

Ionic and Organometallic-Catalyzed Organosilane Reductions

Gerald L. Larson • James L. Fry

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GERALD L. LARSON and JAMES L. FRY



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FOREWORD

Chemical synthesis is an intellectually and technically challenging enterprise. Over the many decades of progress in this discipline, spectacular advances in methods have made once intimidating transformations now routine. However, as the frontier advances and the demands for ready access to greater molecular complexity increases, so does the sophistication of the chemical reactions needed to achieve these goals. With this greater sophistication (and the attendant expectation of enhanced generality, efficiency, and selectivity) comes the challenge of adapting these technologies to the specific applications needed by the practitioner. In its 67-year history, *Organic Reactions* has endeavored to meet this challenge by providing focused, scholarly, and comprehensive overviews of a given transformation.

By any yardstick, the reduction of organic compounds is one of the most important methods for the manipulation of functional groups. No fewer than 27 of the 245 chapters in the *Organic Reactions* series are dedicated to reduction in one if its manifold forms. Among the mildest of these transformations is the use of ubiquitous organosilanes. Because of the wide range of organosilanes available and the different mechanisms by which they can be activated to transfer the hydride, these reagents have found extensive application in organic synthesis. A startling array of different functional groups can be reduced by organosilanes with high selectivity. The oxidized organosilane byproducts are easily removed and non-toxic. Moreover, some of the most exciting recent developments involve the enantioselective reduction of double-bonded functional groups.

The *Organic Reactions* series is fortunate to have published a timely chapter on this important process that single-handedly constituted Volume 71. This comprehensive chapter was authored by two of the internationally recognized leaders in this field, Dr. Gerald L. Larson and Prof. James L. Fry. Although many reviews and book chapters have been written on reductions with organosilanes, this massive work constitutes the definitive treatise in the field. Thus, in keeping with our educational mission, the Board of Editors of *Organic Reactions* has decided to publish this chapter as a separate, soft cover book to make the work available to a wider audience of chemists. In addition, to keep pace with the rapid development of this field, Drs. Larson and Fry have provided updated references that bring the literature coverage up to March 2009. These references are appended at the end of the original reference section and organized by the Tabular presentation of the different substrates for reduction.

The publication of this book represents the third soft cover reproduction of single-volume *Organic Reactions* chapters. The success of the first two soft cover

books (“The Stille Reaction” taken from Volume 50 and “Handbook of Nucleoside Synthesis” taken from Volume 55) has convinced us that the availability of low-cost, high-quality publications that cover broadly useful transformations is addressing an unmet need in the organic synthesis community. Thus we will continue to identify candidates for the compilation of such individual volumes as opportunities present themselves.

Scott E. Denmark
Urbana, Illinois

PREFACE

The reduction of organic functional groups ranks as one of the most important transformations in synthetic organic chemistry. The range of reagents for organic reductions spans from the highly-reactive, highly-nucleophilic metal hydrides at one extreme, to the inert dihydrogen molecule at the other. In view of the variety of organic functional groups that are subject to reduction, highly selective reducing agents are needed. Organosilanes are particularly well suited to meet this challenge because they can be electronically and sterically modified to finely tune their reactivity and thus achieve a number of chemoselective reductions. The substrates in ionic organosilane reductions require activation by an acid or organometallic catalyst. Thus, the reaction selectivity can be further optimized by the choice of activator. Organosilane reduction of essentially all reducible organic functional groups including aromatic rings, aryl halides, carboxylic acids, and amides have been achieved. Moreover, the use of chiral ligands and chiral organometallic catalysts in conjunction with organosilanes has allowed the enantioselective reduction of ketones, imines, enamines, enones, enals, and α,β -unsaturated esters with extremely high selectivities.

Experimental reaction conditions are discussed and numerous specific experimental procedures are provided from the literature for a wide spectrum of representative functional group transformations using this method. A tabular survey of all examples of organosilicon hydrides used in organic synthesis is presented in 34 tables organized by type of substrate reduced with listings within each table according to increasing carbon number of the substrates.

The literature is covered through March 2009, supplementing the coverage used in the earlier hard cover chapter. These latest literature references have been collected in separate sections according to the sequence of the tables in the tabular survey section. In each of the sections, the individual citations have been arranged in alphabetic order of the author names.

Ionic and Organometallic-Catalyzed Organosilane Reductions is intended to be a useful, easily read tool for all practitioners of organic synthesis.

IONIC AND ORGANOMETALLIC-CATALYZED ORGANOSILANE REDUCTIONS

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INTRODUCTION

The purpose of this chapter is to present a critical review of synthetically useful variations of ionic methods for hydrogenation of organic compounds. In practice, ionic hydrogenation involves the formal introduction of hydride from a donor source to an electron-deficient carbon center. The electrophilic centers can be formed by the departure of a leaving group (nucleofuge) from a saturated center or by the addition of an electrophile to a multiple bond. In the former mechanism, substitution of hydrogen for the leaving group is the net chemical consequence. In the latter, addition across the multiple bond is the result.

In this chapter, we cover the use of organosilicon hydrides as the source of ionic hydride with the goal of completing and updating earlier review works on the subject.¹⁻⁴ Similar chemistry is observed when molecular hydrogen^{5,6} or various hydrocarbons⁷⁻⁹ are used as hydride sources; these methods have been reviewed previously and are not covered herein. The use of organosilicon hydride-metal catalyst mixtures¹⁰⁻¹² for effecting reductions is included in this review, but use of trichlorosilane-tertiary amine combinations¹³ is not.

Organosilicon compounds with at least one Si-H bond (called hydrosilanes, organosilicon hydrides, or simply silanes) have the ability to serve as mild air- and water-stable sources of hydride and thus have reducing properties. For example, triethylsilane is reported to reduce a variety of inorganic metal salts directly to the free metals.^{14,15} Even the hexachloroantimonate anion can be reduced to Sb(0) upon contact with this silane.¹⁶ Organotellurium chlorides are reduced to tellurium metal by a number of organosilicon hydrides.¹⁷ Reaction of organosilicon hydrides with strong Brønsted acids leads to decomposition of the silane and the production of hydrogen gas.¹⁴ In general, organosilicon hydrides do not undergo spontaneous reactions with organic compounds unless the organic substrate is a reasonably strong electrophile or the silane has been first activated by the interaction of a nucleophilic species with the silicon center. The organosilicon hydrides are covalent compounds that have little or no nucleophilic properties of their own. Aside from the parent silane, SiH₄, which is pyrophoric, the organosilicon hydrides are fairly innocuous compounds whose physical properties bear resemblance to their hydrocarbon analogs. Thus, their physical and chemical reducing properties differ from those of many familiar metal hydride reducing agents.^{18,19} The use of organosilicon hydrides often provides a means of effecting reductions of organic substrates under very mild conditions and with excellent functional group selectivity.

Consideration of the nature of the Si-H bond provides insight into the chemical behavior of organosilicon hydrides. Comparison of the bond strengths as

represented by bond dissociation energy (BDE) of hydrosilanes with those of hydrocarbon analogs shows that, in general, the Si–H bond is not much weaker than the C–H bond. Thus, the BDE values for the respective Si–H bonds in TMS–H and $(\text{C}_2\text{H}_5)_3\text{Si–H}$ are 90.3²⁰ and 90.1 kcal/mol²¹ compared with a value of approximately 92 kcal/mol²⁰ for the tertiary C–H bond in $(\text{CH}_3)_3\text{C–H}$. On the other hand, there is a significant difference between the polarization characteristics of the Si–H and C–H bonds.²² Compared to the Pauling electronegativity of hydrogen (2.20), the electronegativity of carbon (2.50) is greater and that of silicon (1.90) is less.²³ Carbon-hydrogen bonds are thus polarized in the direction $\text{C}^{\delta-}\text{–H}^{\delta+}$, whereas Si–H bonds are $\text{Si}^{\delta+}\text{–H}^{\delta-}$. As will be seen, this enhanced hydridic nature manifests itself in the chemical behavior of essentially all hydrosilanes.

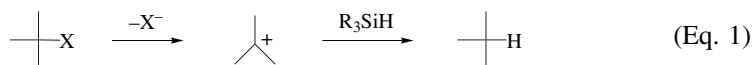
Limited studies of the germanium and tin hydride analogs of the silicon hydrides show that they share this ability to function as hydride sources in ionic hydrogenations; however, their relatively greater reactivity toward acids appears to restrict their practical applications in organic synthesis.^{24,25}

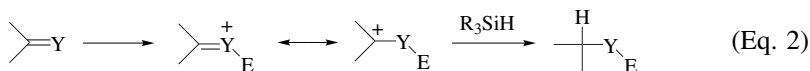
MECHANISM

General Considerations

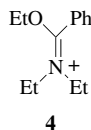
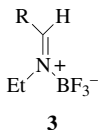
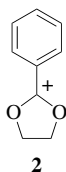
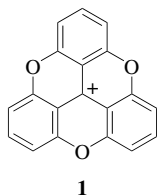
The mechanistic discussion of silane reductions will be limited to those of cationic reductions, thus excluding the many silane reductions that involve metal catalysis.

Since tetravalent organosilicon hydrides intrinsically lack nucleophilicity, they react only with atomic centers that are substantially electron deficient, for example, carbocations. Because of this, organosilicon hydride reductions are potentially very selective. The “ionic” reductions of organic compounds by organosilicon hydrides are understood on the basis of two mechanisms. In the first, substitution by hydrogen of a leaving group bonded to a saturated carbon occurs. This path may be called a σ -route as it involves the stepwise cleavage of a σ -bond to a saturated center and the intervention of a carbocation intermediate that is captured by donation of hydride from the organosilicon hydride (Eq. 1). Alternatively, addition of an electrophile/hydride pair takes place across a multiple bond. This path may be termed a π -route (Eq. 2). Complexation of an electrophile to one end of a π -bond is followed by capture of the intermediate cation or complex by organosilicon hydride. The electrophile may be as simple as a proton or be one of a variety of Lewis acids or alkylating agents. The group Y can be C, O, N, or S. Sometimes the product of Eq. 2 can continue reacting by way of Eq. 1, with the moiety Y–E acting as a leaving group. When this occurs, the net effect is to replace the $\text{C}=\text{Y}$ functionality with CH_2 . The normal caveats regarding carbocation behavior such as the possible occurrences of eliminations, skeletal isomerizations, and bimolecular reactions prior to capture by hydride must be expected in all of these scenarios.





It is necessary for the intermediate cation or complex to bear considerable carbocationic character at the carbon center in order for effective hydride transfer to be possible. By carbocationic character it is meant that there must be a substantial deficiency of electron density at carbon or reduction will not occur. For example, the sesquioxanthryl cation **1**,²⁶ dioxolenium ion **2**,²⁷ boron-complexed imines **3**, and O-alkylated amide **4**,²⁸ are apparently all too stable to receive hydride from organosilicon hydrides and are reportedly not reduced (although the behavior of **1** is in dispute²⁹). This lack of reactivity by very stable cations toward organosilicon hydrides can enhance selectivity in ionic reductions.

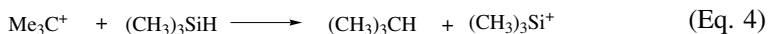


Role of Trivalent Silicon Species

The overall stoichiometry of hydride transfer from a silicon center to an electron-deficient carbon center is quite straightforward. Almost without exception, it appears that there is simple interchange of hydride to the carbocation while the silicon center receives the elements of the carbocation's counterion (Eq. 3).



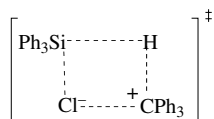
When the counterion is complex, for example metal-halogen anions such as BF_4^- , the most electronegative portion of the counterion becomes attached to the silicon center. Because of this attachment, it is natural to consider the intermediacy of a silicenium cation (silylium or silylenium ion) intermediate in such reactions (Eq. 4). Bond energies derived from electron impact studies indicate that Eq. 4 is exothermic in the gas phase by about 8 kcal/mol.^{26,29} There seems little doubt that trivalent silicon-centered cationic species do exist in the gas phase^{30,31} or that processes similar to that shown in Eq. 4 do occur there.^{32,33}



The existence of trivalent silicenium cations as reactive species in solution is more controversial. Many early attempts to demonstrate the solution-phase existence of stable silicenium ions by using techniques analogous to those successfully applied to carbocation formation failed.³⁴⁻³⁶ Other reports of attempts

to generate silicenium ions in solution under stable ion conditions³⁷⁻⁴⁶ and in solvolyses⁴⁷ are more convincing, but not without controversy.⁴⁸⁻⁵¹ The single-crystal X-ray determination of a non-planar triethylsilylium moiety paired in the crystalline state with the tetrakis(pentafluorophenyl)borate gegenion and toluene solvate stirred much debate about its interpretation and extension to reaction systems.^{52,53} Recent crystallographic evidence supports the notion of a three-coordinate structure of a trimesitylsilylium cation paired with a carborane anion in the solid phase.^{54,55} The balance of experimental evidence seems to indicate that, whereas trivalent silicenium cations may have fleeting existence as reaction intermediates, it is unlikely that they exist as stable, long-lived species in solution.⁵⁶ The failure to observe such trivalent species in solution is related to the very strong ability of electron-deficient silicon centers to coordinate with the media in which they are formed.^{53,57,58} This is true even in solvents that exhibit little or no nucleophilicity toward carbocations and is further enhanced by the relatively long bond lengths to silicon centers that allow a close approach by coordinating species.⁵³

The available experimental information is suggestive, but not unambiguously conclusive, of the intervention of electron-deficient silicon-centered species that may resemble silicenium cations in simple hydride exchanges occurring in solvents with low coordinating abilities. For example, substituted triarylmethane derivatives such as chlorotriphenylmethane (trityl chloride) undergo reduction through halogen-hydride exchange with organosilicon hydrides. The reactions proceed more rapidly in solvents with high ionizing power, but are kinetically first order with respect to both organosilicon hydride and triarylmethane derivative in benzene solvent.⁵⁹ In benzene, the exchange of halogen with hydride occurs with retention of configuration at the silicon center.⁶⁰ These results have led to the suggestion that the exchanges proceed by way of a four-center transition state **5**, in which there is simultaneous attack by the halide of the carbocation-halide ion pair on the silicon center as hydride undergoes transfer to the carbocation center.⁶⁰



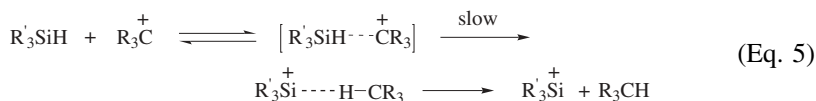
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Simple variation of the solvent has a very significant effect on the stereochemistry at the silicon center for these exchange reactions. The stereochemistry changes from essentially complete retention to inversion and even to racemization. For example, in dichloromethane the halogen is delivered to the silicon center with complete racemization.⁶¹ This implies that the degree of "tightness" of the carbocation-counterion pair must change depending on the solvent.

Organosilicon hydride reductions of preformed stable carbocations such as triphenylmethyl (trityl) tetrafluoroborate and hexafluoroantimonate salts are rapid

and essentially quantitative.^{62,63} Reductions of these and similar stable ions in dichloromethane/trifluoroacetic acid (TFA) show primary deuterium kinetic isotope effects in the range $k_H/k_D = 1.27^{64}$ to 1.89^{65} at room temperature, whereas effects equal to $k_H/k_D = 1.50$ – 2.33 are seen for the reduction of diarylcarbenium ions with deuteriosilanes at -70° .⁶⁶ The kinetic rate dependence for similar reactions in acetic acid is first order in both the cation and the silane. The rates of a series of substituted arylsilanes correlate with σ constants, but not with σ^+ constants, to produce Hammett plots with $\rho = -1.84$ for triarylsilanes and $\rho = -1.01^{65}$ to -2.46^{66} for aryldimethylsilanes. These results are interpreted to mean that the reactions occur through a four-center transition state in which the silicon center assumes a trigonal-bipyramidal shape with hydride exiting from an equatorial position while the carbocation's counterion approaches axially.⁶⁵

Trityl and tropylium (cycloheptatrienyl) cation salts having complex metal-halide anions such as SbX_6^- , AsF_6^- , PF_6^- , FeCl_4^- , and BF_4^- undergo reduction with trialkylsilanes and aryldialkylsilanes at rates that are independent of the nature of the anion or of ring strain in the organosilicon hydride, are kinetically first order with respect to both cation and organosilicon hydride, and that display primary deuterium kinetic isotope effects of $k_H/k_D = 1.41$ – 1.49 in dichloromethane.^{67,68} It is argued that these reactions proceed by way of a three-step mechanism involving a rate-determining single-electron transfer step⁶⁹ to create a charge-transfer complex between the carbocation and the organosilicon hydride followed by a faster transfer of hydride to the carbon center and the creation of a silenium ion intermediate that is then rapidly captured by the counterion present (Eq. 5).⁶⁸ Others regard this argument as doubtful compared to the polar mechanism in which Si–H bond cleavage is rate determining.⁶⁶

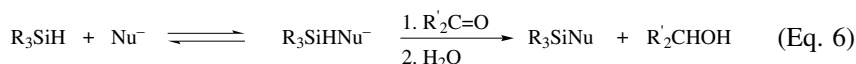


Uncertainties in understanding the exact mechanistic details of these reactions are sure to stimulate continued work to define the nature of trivalent silicon cations in ionic reductions by organosilicon hydrides.

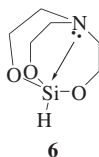
Role of Hypervalent Silicon Species

It is well known that strong electrophiles such as carbocations are reduced by organosilicon hydrides (Eq. 1).^{3,70,71} On the other hand, simple mixtures of organosilicon hydrides and compounds with weakly electrophilic carbon centers such as ketones and aldehydes are normally unreactive unless the electrophilicity of the carbon center is enhanced by complexation of the carbonyl oxygen with Brønsted acids^{3,70–73} or certain Lewis acids (Eq. 2).^{1,70,71,74,75} Using these acids, hydride transfer from the silicon center to carbon may then occur to give either alcohol-related or hydrocarbon products.

Alternatively, unreactive mixtures of organosilicon hydrides and carbonyl compounds react by hydride transfer from the silicon center to the carbon center when certain nucleophilic species with a high affinity for silicon are added to the mixture.^{76–94} This outcome likely results from the formation of valence-expanded, pentacoordinate hydrosilanide anion reaction intermediates that have stronger hydride-donating capabilities than their tetravalent precursors (Eq. 6).^{22,95–101}



The bicyclic silatrane molecule **6**, which has a strong degree of coordination between the silicon center and the nitrogen bridgehead, has been shown to have unusually strong reducing properties compared to normal tetravalent organosilicon hydrides.¹⁰² The hypothesis that valence-expanded pentacoordinate silicon species are the actual reducing species^{76,77,83} is plausible, for such species are well known.^{96,99,101,103–107} Other examples are known of the enhanced reducing powers of organosilicon hydrides that undergo intramolecular coordination and expansion to pentavalent⁸² and even hexavalent states.^{84,101,108–111}



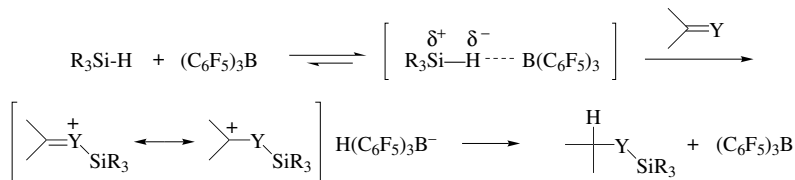
A variety of nucleophilic species cause valence expansion of organosilanes and the enhancement of reducing reactivity. These include formate, thiocyanate, tartrate, and phthalate salts,⁷⁸ as well as alkoxides^{91,92,96,99,107} and catecholates.⁹³ The strong propensity of fluoride ion to cause silicon centers to undergo valence expansion^{95,112} makes it especially effective in activating organosilicon hydrides as reducing agents. Aldehydes, ketones, and esters may all be reduced by such a technique, frequently with excellent functional group and stereochemical selectivity.^{76–89}

The valence-expanded silicon intermediate retains some measure of stereochemical integrity up to the point of hydride transfer as evidenced by the small degrees of asymmetric induction that are observed in the reduction of prochiral ketones coupled with similar degrees of chirality found at the silicon center.⁸⁵ The transfer of hydride from the silicon center to the carbonyl carbon takes place in the rate-determining step as judged by the primary deuterium kinetic isotope effect of 1.50 observed in the fluoride-induced reduction of acetophenone with dimethylphenylsilane-*d*₁.⁸⁸ There is also evidence that the pentacoordinate silicon hydride can serve as a single-electron-transfer donor since radical-coupling products are sometimes obtained, although the general importance of this process is open to question.^{89,99}

A diaryldihydrosilane with a hexacoordinated silicon center, produced through intramolecular coordination, is reported not to react with benzaldehyde, although the silane is capable of reducing silver ion to silver metal.¹¹³ There is also a report of a heptacoordinate silicon hydride species with the ability to transfer hydride to trityl cation while remaining inactive toward methanol.^{108,114}

Role of O/N-Silylated Cationic Intermediates

An interesting variation of the reaction mechanisms discussed above has been offered following studies of the hydrosilation reductions of aldehydes, ketones, and esters to their corresponding silyl ethers and acetals, respectively, when catalyzed by tris(pentafluorophenyl)borane, $(\text{C}_6\text{F}_5)_3\text{B}$,^{115,116} and related boranes.¹¹⁷ This mechanism proposes a pathway in which the first step is the reversible formation of a linear silane-borane adduct that undergoes subsequent nucleophilic attack by the carbonyl compound of the substrate to yield an O-silylated cationic intermediate along with a boron hydride anion.¹¹⁸ The boron hydride ion then transfers a hydride to the carbon center of the O-silylated cation to yield the reduction product and regenerated free borane. A simplified view of the suggested mechanism is shown below (Scheme 1). Similar reaction paths have been proposed for the hydrosilation of enones and silyl ethers¹¹⁹ as well as imines.¹²⁰



Scheme 1

Role of Metal Catalysts

A wide variety of metals can effectively catalyze the reduction of multiple bonds by organosilicon hydrides (Eq. 2). No doubt, the function of some of these metals is to serve as Lewis acids by adding to the most electron-rich end of a bond and promoting transfer of hydride to the other center. On the other hand, it is clear that many transition metal complexes function through significantly different and more complex catalytic pathways to promote silane reductions. A common reaction stage suggested for many of the catalytic cycles is the creation of a reactive intermediate having a metal-hydrogen bond that is formed by hydrogen transfer from the silane to the catalytic metal center.¹¹⁶ This reducing center, often with appropriate coordinating ligands, subsequently delivers hydrogen to the substrate and the metal center is freed for additional catalytic cycles. When the catalytic metal ligands are chiral, this process can lead to very high degrees of enantiomeric selectivity in the reduction of prochiral substrates.¹²¹⁻¹²⁵

SCOPE AND LIMITATIONS

Reduction of Substituted Alkanes

Alcohols to Alkanes. Many alcohols are converted directly into hydrocarbons when treated with acid in the presence of organosilicon hydrides (Eq. 7). The mechanism normally follows the pathway shown in Eq. 1.



The reaction generally proceeds cleanly and in high yields (70–100%) when the starting alcohol permits the formation of reasonably stable carbocation intermediates. Alcohols capable of producing carbenium ions spanning a range of stabilities of more than 24 pK_{R+} units undergo this reduction.²⁶ Depending on the reaction conditions, secondary¹²⁶ and tertiary¹²⁷ aliphatic alcohols, secondary and tertiary benzylic alcohols,^{26,126} some ring-substituted primary benzylic alcohols,^{26,128,129} and cyclopropylcarbinols¹³⁰ are reduced to the corresponding alkanes. However, olefinic and rearrangement products can occur from side reactions under these acid conditions.^{126,131,132} Phenols are not reduced under the same conditions.

Almost any organosilicon hydride causes reduction of the cations produced, although the order of reactivity of simple alkyl and aryl-substituted silanes is observed to be triethyl > trioctyl ~ diethyl > diphenyl ~ triphenyl.²⁶ A detailed quantitative study of the reactions of organosilicon hydrides with diarylcarbenium ions in dichloromethane at –70° indicates a relative reactivity order of R₃SiH > R₂SiH₂ > RSiH₃, with alkyl substituent groups generally producing greater reactivity than aryl substituents.⁶¹ Use of a deuterated silane yields the corresponding deuterated hydrocarbon (Eq. 8).^{127,133,66}



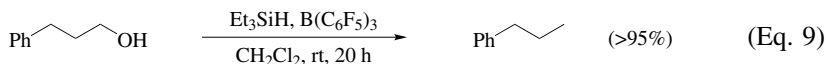
Normally, only a small stoichiometric excess (2–30 mol%) of silane is necessary to obtain good preparative yields of hydrocarbon products. However, because the capture of carbocation intermediates by silanes is a bimolecular occurrence, in cases where the intermediate may rearrange or undergo other unwanted side reactions such as cationic polymerization, it is sometimes necessary to use a large excess of silane in order to force the reduction to be competitive with alternative reaction pathways. An extreme case that illustrates this is the need for eight equivalents of triethylsilane in the reduction of benzyl alcohol to produce only a 40% yield of toluene; the mass of the remainder of the starting alcohol is found to be consumed in the formation of oligomers by bimolecular Friedel-Crafts-type side reactions that compete with the capture of the carbocations by the silane.¹²⁹

Both Brønsted and Lewis acids are effective in coordinating with the hydroxyl oxygen to induce heterolysis of the C–O bond and cause formation of the necessary carbocation intermediate. The reactions are frequently conducted

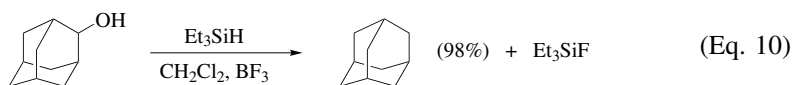
under homogeneous conditions in inert solvents such as dichloromethane or chloroform. Conditions used include the treatment of alcohols with organosilicon hydrides in neat acetic acid,^{26,29} neat trifluoroacetic acid¹³⁴ or trifluoroacetic acid/ammonium fluoride¹³⁵ as well as mixtures of trifluoroacetic acid,²⁶ methanesulfonic acid,¹²⁶ or triflic (trifluoromethanesulfonic) acid with triflic anhydride¹²⁶ in dichloromethane or chloroform, mixtures of acetic acid and sulfuric or *p*-toluenesulfonic acid,¹³⁴ acetic acid and hydrogen chloride/aluminum chloride,¹³⁶ and boron trifluoride¹²⁶ or boron trifluoride etherate in dichloromethane^{137,133} or chloroform.¹³⁸ The use of very strong Brønsted acids such as methanesulfonic and triflic acids may cause decomposition of the organosilane through hydrogen production¹⁴ and/or cleavage of Si–C bonds¹³⁹ which compete with the desired reduction of the alcohol.¹²⁶ These undesirable side reactions may be avoided or reduced by running the reaction at -78° .¹⁴⁰ Sulfuric acid may cause undesirable oxidations to occur.¹³⁴ On balance, the most commonly chosen set of conditions for the reduction of alcohols is triethylsilane and trifluoroacetic acid ($\text{Et}_3\text{SiH/TFA}$) in dichloromethane solution.

The experimental evidence is convincing, at least with benzyl alcohols, that a “free” carbenium ion intermediate devoid of influence from its progenitor is the species that is captured by the non-nucleophilic organosilicon hydride. When optically active 2-phenyl-2-butanol is treated with $\text{Et}_3\text{SiH/TFA}$ in chloroform, the 2-phenylbutane product is formed with complete racemization.²⁶ When a dichloromethane solution of the same alcohol is treated with trifluoroacetic acid in the presence of enantiomerically enriched 1-naphthylphenylmethylsilane, the 2-phenylbutane product obtained shows a small, but reproducible enantiomeric excess of 2–3%.¹⁴¹ The predominant enantiomer formed in the product is dependent only on the predominant enantiomer of silane used as the reducing agent and is independent of whether one of the pure enantiomers or the racemic alcohol is used as substrate.¹⁴² The same stereochemical results are obtained in the hydrocarbon product when the alkene 2-phenyl-1-butene is the precursor to the carbenium ion intermediate (π -route, Eq. 2) instead of the tetrahedral alcohol (σ -route, Eq. 1).¹⁴² A similar conclusion is reached from a study of the reduction of optically active 1-phenylethanol to phenylethane- d_1 with boron trifluoride etherate and triethylsilane- d_1 .¹³³ These experiments illustrate the lack of nucleophilicity or S_N2 -like behavior of the organosilicon hydrides in these reactions and presage the stereochemistry expected from such transformations.

Primary Alkyl Alcohols. Primary alkyl alcohols do not undergo reduction when treated with Brønsted acids and organosilicon hydrides under usual laboratory conditions.¹⁴³ This reflects the relative instability of primary alkyl carbenium ions in the condensed phase and the weak intrinsic nucleophilicity of organosilicon hydrides. On the other hand, the combination of excess Et_3SiH and catalytic amounts (5–10 mol%) of $(\text{C}_6\text{F}_5)_3\text{B}$ reduces primary aliphatic alcohols to the alkanes in high yields (Eq. 9), but the reaction stops at the non-reductive silylation of the alcohol with only a single equivalent of the silane.^{144,145} This type of reaction is thought to proceed via a direct nucleophilic displacement rather than by way of a carbenium ion mechanism.¹⁴⁵

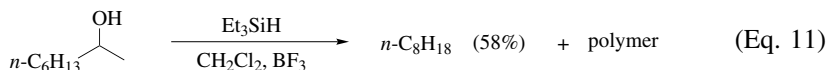


Secondary Alkyl Alcohols. Treatment of secondary alkyl alcohols with trifluoroacetic acid and organosilicon hydrides results only in the formation of the trifluoroacetate esters; no reduction is reported to occur.^{1,2} Reduction of secondary alkyl alcohols does take place when very strong Lewis acids such as boron trifluoride^{126,129} or aluminum chloride^{136,146} are used. For example, treatment of a dichloromethane solution of 2-adamantanol and triethylsilane (1.3 equivalents) with boron trifluoride gas at room temperature for 15 minutes gives upon workup a 98% yield of the hydrocarbon adamantane along with fluorotriethylsilane (Eq. 10).¹²⁹



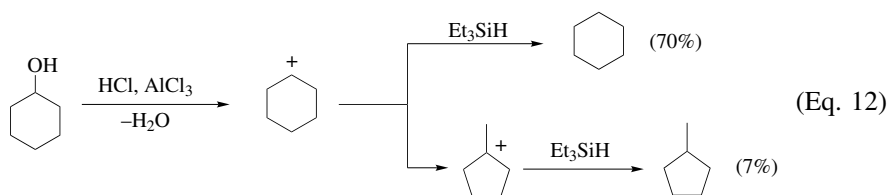
In contrast, when boron trifluoride etherate is substituted for the free boron trifluoride, only a trace of the hydrocarbon is formed, even after weeks of reaction.¹⁴³ The unique effectiveness of boron trifluoride gas in promoting these reductions is believed to be due to several factors, including the ability of the coordinatively unsaturated boron center to rapidly and tightly coordinate with oxygen centers and to the thermodynamically favorable creation of a Si-F bond.¹ A slight pressure of boron trifluoride gas must be maintained over the surface of the solution throughout the reaction because boron trifluoride has only limited solubility in the weakly coordinating dichloromethane solvent.

The formation of alkenes and alkene-related polymerization products can seriously reduce the yields of desired alkane products from secondary alcohols, which can undergo elimination reactions. For example, reduction of 2-octanol at 0° with boron trifluoride gas in dichloromethane containing 1.2 equivalents of triethylsilane gives only a 58% yield of *n*-octane after 75 minutes (Eq. 11).¹²⁹ The remainder of the hydrocarbon mass comprises nonvolatile polymeric material.¹²⁶



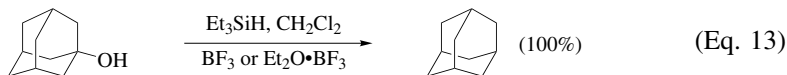
Aluminum chloride, used either as a stoichiometric reagent or as a catalyst with gaseous hydrogen chloride, may be used to promote silane reductions of secondary alkyl alcohols that otherwise resist reduction by the action of weaker acids.¹³⁶ For example, cyclohexanol is not reduced by organosilicon hydrides in the presence of trifluoroacetic acid in dichloromethane, presumably because of the relative instability and difficult formation of the secondary cyclohexyl carbocation. By contrast, treatment of cyclohexanol with an excess of hydrogen chloride gas in the presence of a three-to-four-fold excess of triethylsilane and 1.5 equivalents of aluminum chloride in anhydrous dichloromethane produces 70% of cyclohexane and 7% of methylcyclopentane after a reaction time of 3.5 hours at

room temperature (Eq. 12).¹³⁶ The cyclohexane is presumably formed by capture of the secondary cyclohexyl cation, whereas the methylcyclopentane must arise from hydride capture of the more stable tertiary methylcyclopentyl cation formed by rearrangement of the cyclohexyl cation.^{147,148} Diminishing the amount of aluminum chloride to only 0.5 equivalents results in no reaction after one-half hour and the formation of only 8% of cyclohexane after four hours reaction time. The reaction proceeds slowly in the absence of hydrogen chloride, producing 53% of cyclohexane and 6% of methylcyclopentane after 16.5 hours using two equivalents of aluminum chloride.



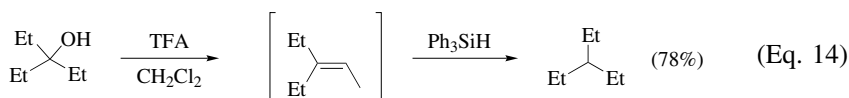
Tertiary Alkyl Alcohols. Tertiary alkyl alcohols generally undergo facile reduction when treated with acids in the presence of organosilicon hydrides.^{127,136} This comparative ease of reduction reflects the enhanced stability and ease of formation of tertiary alkyl carbenium ions compared with primary and secondary carbenium ions. Thus, treatment of 1-methylcyclohexanol with mixtures of triethylsilane and aluminum chloride in dichloromethane produces near quantitative yields of methylcyclohexane with or without added hydrogen chloride in as little as 30 minutes at room temperature, in contrast to the more vigorous conditions needed for the reduction of the secondary alcohol cyclohexanol.¹³⁶

Similarly, and in contrast to the behavior of its secondary isomer, 2-adamantanol, 1-adamantanol undergoes smooth, quantitative reduction to adamantane in less than an hour at room temperature in dichloromethane solution containing triethylsilane under the catalysis of either free boron trifluoride¹²⁹ or boron trifluoride etherate (Eq. 13).¹⁴³

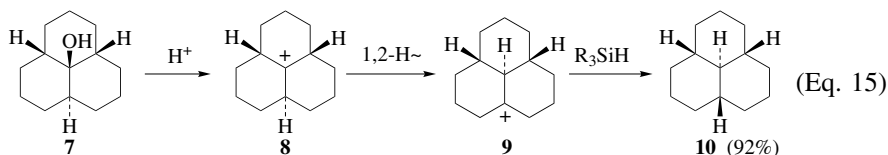


Although the synthetic yields of hydrocarbon products obtained from the reduction of tertiary alkyl alcohols are frequently quite high, studies show that the reaction pathways taken by the reactants are not always as direct or straightforward as might be suggested by the structural relationships between reactants and products. For example, preparative-scale treatment of a dichloromethane solution of 3-ethylpentan-3-ol and triphenylsilane (1.2 equivalents) with excess trifluoroacetic acid (1.5 M) at room temperature for 24 hours gives 3-ethylpentane in 78% yield (Eq. 14).¹²⁷ Under these reaction conditions, the alcohol rapidly

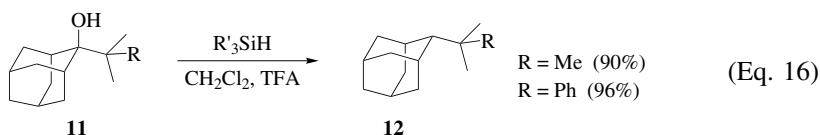
undergoes elimination to 3-ethyl-2-pentene, which is the actual species undergoing reduction.



The tertiary alcohol *cis,cis,trans*-perhydro-9*b*-phenalenol (**7**) is converted stereospecifically and in high yield (92%) to *trans,trans,trans*-perhydrophenalene (**10**) when treated with either triethylsilane or triphenylsilane and trifluoroacetic acid in dichloromethane (Eq. 15). Studies indicate that the reaction path follows the cation rearrangement **8** → **9** and that the *trans* trifluoroacetate ester related to cation **9** is an intermediate, which accumulates during the reaction.¹²⁷

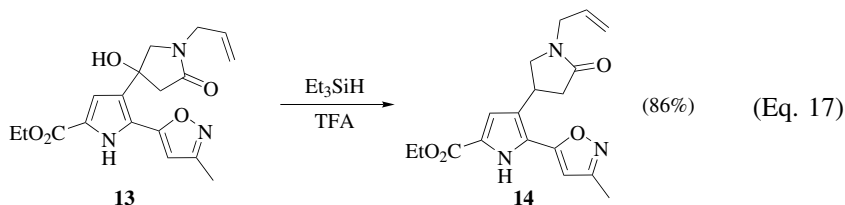


The conversion of alcohols directly into the structurally related hydrocarbons by ionic hydrogenation can provide a means of synthesis for compounds that would be extremely difficult or impossible to obtain by other methods. A good example is the synthesis of 2-*tert*-butyladamantane (**12**, R = Me). This interesting, highly strained compound may be synthesized in moderate overall yield by a conventional multiple-step route.¹⁴⁹ Alternatively, it is obtained in 90% isolated yield upon treatment of a dichloromethane solution of the readily available 2-*tert*-butyl-2-adamantanol (**11**, R = Me)¹⁵⁰ and one equivalent of either tri-*n*-hexylsilane^{151,152} or triethylsilane¹⁵³ with trifluoroacetic acid at room temperature (Eq. 16).

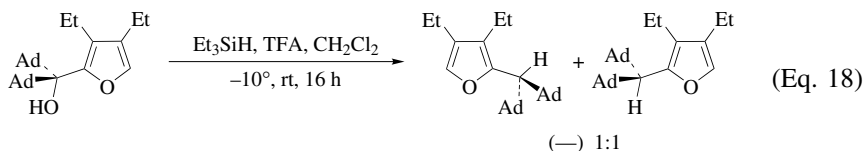


In a similar fashion, 2-cumyladamantane (**12**, R = Ph) is formed in nearly quantitative yield upon treatment of the easily synthesized 2-cumyl-2-adamantanol (**11**, R = Ph)¹⁵⁴ with triethylsilane and methanesulfonic acid in dichloromethane at -78° .¹⁵⁵ The high yield of a single very strained hydrocarbon product in each reaction is quite surprising in view of the very complex interconversions of carbocations known to take place from the alcohol precursors.^{140,151,152,156}

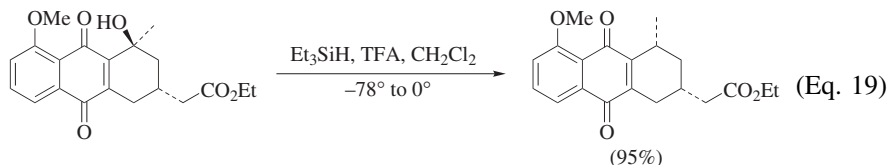
The remarkable chemoselectivity of this reductive technique is demonstrated by the conversion of the functionally rich compound **13** into **14** in 86% yield upon treatment with Et₃SiH/TFA at room temperature for two hours (Eq. 17).¹⁵⁷



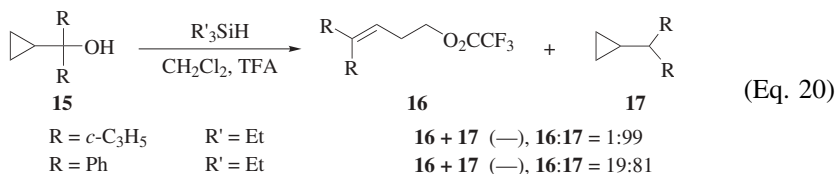
Several sterically congested aryldiamantylmethanols are reduced to atropisomeric diastereomeric mixtures of the corresponding aryldiamantylmethanes with $\text{Et}_3\text{SiH/TFA}$ (Eq. 18).^{158–161}



This reagent combination reduces a tertiary alcohol in the presence of a quinone moiety (Eq. 19).¹⁶² Tertiary alcohols are also reduced with the reagent combinations $\text{Et}_3\text{SiH/MeSO}_3\text{H}$ ¹⁴⁰ and $\text{Et}_3\text{SiH/AlCl}_3/\text{HCl}$.¹³⁶



Cyclopropylcarbinols. Treatment of cyclopropylcarbinols **15** ($\text{R} = \text{Ph}$, $c\text{-C}_3\text{H}_5$) with trifluoroacetic acid in dichloromethane leads to the rapid formation of ring-opened 4-substituted 3-butenyl-1-trifluoroacetate esters **16** (Eq. 20).¹³⁰ Cyclopropylcarbinyl trifluoroacetates are not formed. Ring opening is facilitated by phenyl substituents. Addition of organosilicon hydrides to the reaction mixture favors the formation of cyclopropylmethanes **17** and suppresses the formation of the ring-opened esters.¹³⁰

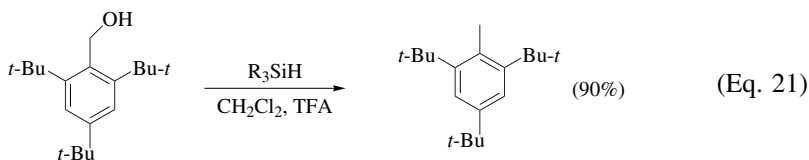


Triethylsilane and diethylsilane are somewhat more effective than triphenylsilane at increasing the amount of reduced product **17**.¹³⁰ Yields of **17** in excess of 90% may be obtained. The remainder of the product is butenyl ester **16**. Hydrogenolysis of the cyclopropyl rings does not occur under these conditions. A better yield of **17** is obtained when the reaction is carried out at -15° than at room

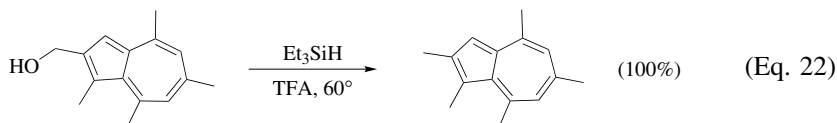
temperature. Under the same set of reaction conditions (dichloromethane, 0.5 M trifluoroacetic acid, 0.5 hour, room temperature), the amount of hydrocarbon product **17** ($R = Ph$) obtained from diphenylcyclopropylcarbinol changes from 16% with triphenylsilane as the hydride-donating reagent to 45% with triphenylgermane, 85% with triphenylstannane, and 78% with tri-*n*-butylstannane.²⁴

Benzyl Alcohols. Benzyl alcohols of nearly all kinds undergo reduction when treated with acid in the presence of organosilicon hydrides. The most obvious exception to this is the behavior of benzyl alcohol itself. It resists reduction by the action of trifluoroacetic acid and triethylsilane, even after extended reaction times.²⁶ Reducing systems consisting of triethylsilane and sulfuric acid/acetic acid or *p*-toluenesulfonic acid/acetic acid mixtures also fail to reduce benzyl alcohol to toluene.¹³⁴ As previously mentioned, substitution of boron trifluoride for trifluoroacetic acid results in the formation of modest yields of toluene, but only when a very large excess of the silane is used in order to capture the benzyl cation intermediate and suppress Friedel-Crafts oligomerization processes.^{129,143}

Ring-substituted benzyl alcohols sometimes undergo such reduction more effectively than unsubstituted alcohols. For example, treatment of a dichloromethane solution of 2,4,6-trimethylbenzyl alcohol with trifluoroacetic acid and triphenylsilane produces a 41% isolated (89% by GLC) yield of isodurene.²⁶ Treatment of 2-methyl-4,6-di-*tert*-butylbenzyl alcohol with a three-fold excess of triethylsilane and trifluoroacetic acid in dichloromethane at room temperature gives an 85% yield of 2-methyl-4,6-di-*tert*-butyltoluene together with 15% of 3,5-di-*tert*-butyltoluene. The latter is presumably formed by loss of protonated formaldehyde from the C1 ring-protonated substrate.¹²⁸ Similar treatment of 2,4,6-tri-*tert*-butylbenzyl alcohol produces a 90% yield of 2,4,6-tri-*tert*-butyltoluene within one hour (Eq. 21).¹²⁸

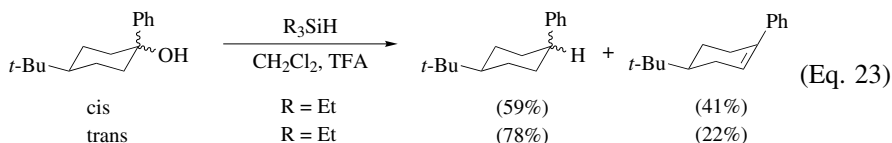


The reduction of 2-(hydroxymethyl)-1,4,6,8-tetramethylazulene to 1,2,4,6,8-pentamethylazulene occurs quantitatively upon treatment with triethylsilane and trifluoroacetic acid at 60° for 19 hours (Eq. 22).¹⁶³

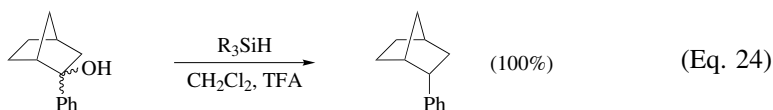


Treatment of either the *cis* or *trans* isomer of 4-*tert*-butyl-1-phenylcyclohexanol with trifluoroacetic acid and one of a variety of organosilicon hydrides in dichloromethane yields a mixture of *cis*- and *trans*-4-*tert*-butyl-1-phenylcyclohexane and the elimination product, 4-*tert*-butyl-1-phenylcyclohexene

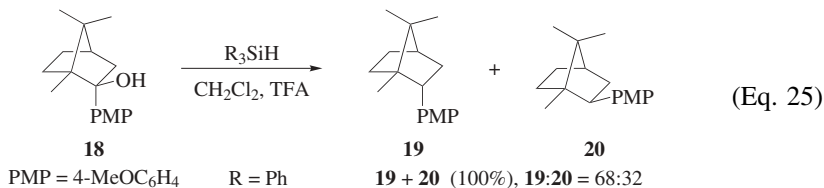
(22–72%) (Eq. 23).²⁶ More elimination product is obtained from the *cis* than from the *trans* alcohol. The *trans/cis* ratio of reduced products is independent of the isomer of starting alcohol used and depends only on the nature of the silane used. This ratio is ca. 1.8 for triorganosilanes (e.g., triethyl, tri-*n*-octyl, triphenyl) and ca. 4.0 for diorganosilanes (e.g., diethyl, diphenyl) and phenylsilane. The most important factor for the stereoselectivity of product formation seems to be the degree of steric bulk provided by the organic groups bonded to silicon, rather than the electronic nature of the substituents. The smaller the effective steric bulk of the reducing agent, the greater is the *trans/cis* product ratio.²⁶ Replacement of the silanes with germanes or stannanes as the hydride donors causes a decrease in the amount of elimination product formed so that it becomes a minor product (10–38%).²⁴ The *trans/cis* ratio of reduced products is ~ 2 when triphenylgermane is used, ~ 1.4 with triphenylstannane, and ~ 0.85 with tri-*n*-butylstannane.²⁴



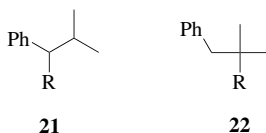
Reduction of either the *exo* or *endo* isomer of 2-phenyl-2-norbornanol with trifluoroacetic acid and triethylsilane, triphenylsilane, or phenylsilane in dichloromethane gives *endo*-2-phenylnorbornane quantitatively (Eq. 24).¹⁶⁴ The stereospecific formation of only the *endo*-hydrocarbon can be understood on the basis that only *exo* approach by organosilicon hydride toward the 2-phenylnorbornyl cation intermediate is kinetically competitive for product formation.¹⁶⁴



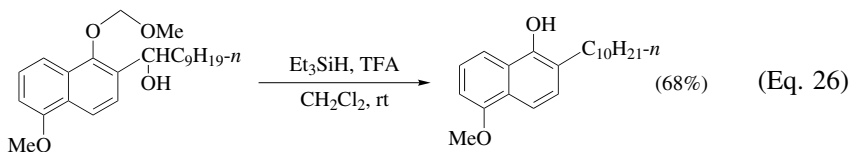
The bornyl system is less subject than the norbornyl system to exclusive *exo* approach by organosilicon hydrides and related reducing agents because of the steric restraints imposed by the additional methyl groups. Thus, treatment of a dichloromethane solution of *p*-anisylisoborneol (**18**) with trifluoroacetic acid and triphenylsilane quantitatively provides the isomeric reduced products *p*-bornylanisole (**19**) and *p*-isobornylanisole (**20**) in a ratio of 68 : 32 (Eq. 25).²⁴ Replacement of the triphenylsilane with triphenylstannane produces 98% of **19** and 2% of **20**. Use of the sterically less demanding phenylsilane gives **19** as the exclusive product. By comparison, trapping of the cation derived from **18** with borohydride gives 87% of **19** and 13% of **20**.¹⁶⁵



Reductions of tertiary or benzylic alcohols do not always take place as quickly and simply as might be expected. A study of the reduction of 2-methyl-1-phenylpropan-1-ol (**21**, R = OH) and its isomer, 2-methyl-1-phenylpropan-2-ol (**22**, R = OH), illustrates this observation.¹⁶⁶ Both of these alcohols are reduced in high yield (98%) by the action of acid and triphenylsilane to the same hydrocarbon, 2-methyl-1-phenylpropane (**21** or **22**, R = H). The immediate products formed from either alcohol in a 55% solution of trifluoroacetic acid in nitrobenzene are the trifluoroacetate esters (R = CF₃CO₂). Surprisingly, at 25° in the absence of organosilicon hydride, ester **21** (R = CF₃CO₂) undergoes complete isomerization to ester **22** (R = CF₃CO₂) within two hours. Use of triphenylsilane-*d*₁ as the reducing agent indicates that alcohol **21** (R = OH) actually produces a mixture of the two isotope-position isomers of the reduction product (**21** and **22**, R = D), with isomer **22** favored by a factor of 2 to 3 over isomer **21**. Similar results are found when the starting alcohol is **22**. The conclusion is reached that the species actually captured by the organosilicon hydride consists of a dynamic mixture of the two cations derived from **21** and **22**.¹⁶⁶

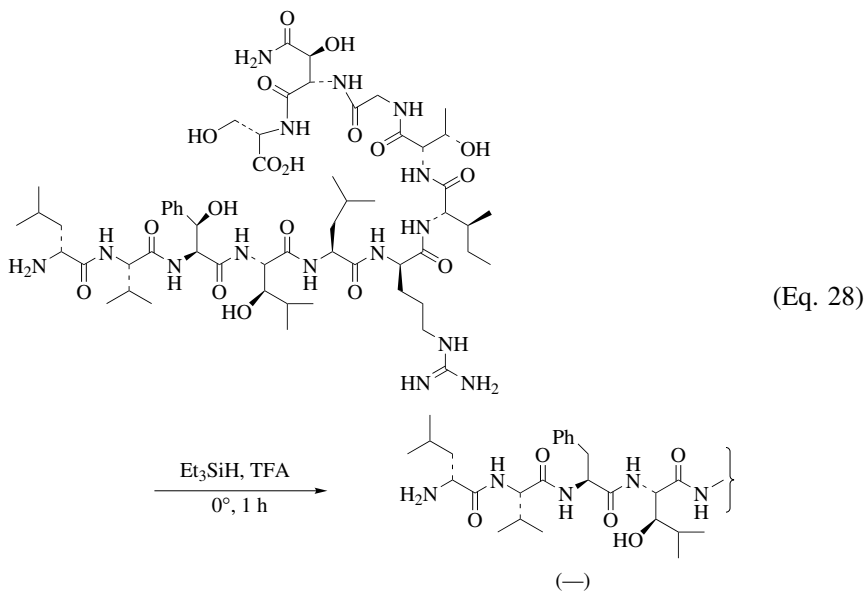
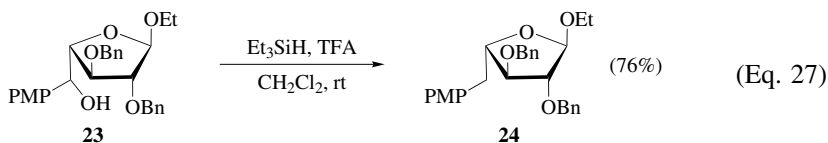


In some instances, treatment of polyfunctional benzylic alcohols with acid in the presence of organosilicon hydrides causes multiple functional group transformations to occur simultaneously. This phenomenon is illustrated by the reduction of the secondary benzylic alcohol function and concomitant loss of the methoxymethyl protecting group of 2-(1-hydroxydecyl)-5-methoxy-1-(methoxymethyleneoxy)naphthalene upon treatment with Et₃SiH/TFA in dichloromethane (Eq. 26).¹⁶⁷



An example of an exclusive chemoselective reduction of a benzylic hydroxy function in a polyfunctional compound is seen in the conversion of **23** into **24**

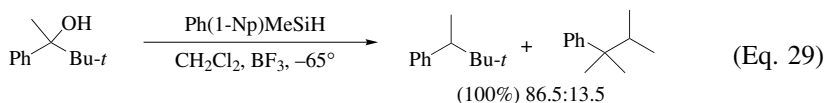
in 76% yield using $\text{Et}_3\text{SiH/TFA}$ (Eq. 27).¹⁶⁸ The benzylic hydroxy group in a complex polypeptide derived from lysobactin is selectively reduced with the same reagents (Eq. 28).¹⁶⁹



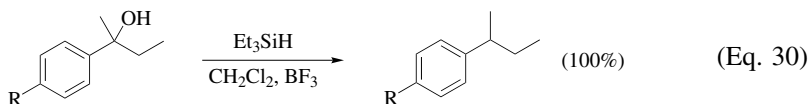
Studies reveal an advantage to using boron trifluoride in dichloromethane at reduced temperatures instead of Brønsted acids in the organosilicon hydride reductions of a number of dialkylbenzyl alcohols.^{126,129} The use of Brønsted acids may be unsatisfactory under conditions in which the starting alcohol suffers rapid skeletal rearrangement and elimination upon contact with the acid, and also in which the alcohol does not yield a sufficient concentration of the intermediate carbocation when treated with protic acids.¹²⁶

An example of an alcohol that can undergo rapid skeletal rearrangement is 3,3-dimethyl-2-phenyl-2-butanol (Eq. 29). Attempts to reduce this alcohol in dichloromethane solution with 1-naphthyl(phenyl)methylsilane yield only a mixture of the rearranged elimination products 3,3-dimethyl-2-phenyl-1-butene and 2,3-dimethyl-3-phenyl-1-butene when trifluoroacetic acid or methanesulfonic acid is used. Use of a 1:1 triflic acid/triflic anhydride mixture with a 50 mol% excess of the silane gives good yields of the unrearranged reduction product 3,3-dimethyl-2-phenylbutane, but also causes extensive decomposition of the silane.¹²⁶ In contrast, introduction of boron trifluoride gas into a dichloromethane solution of the alcohol and a 10 mol% excess of the silane

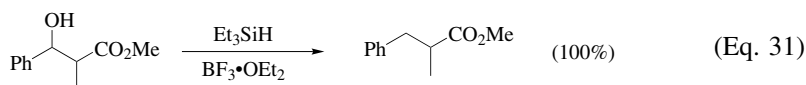
at -60° produces 86.5% of the desired, structurally intact hydrocarbon, 3,3-dimethyl-2-phenylbutane, along with 13.5% of the methyl-shifted product, 2,3-dimethyl-2-phenylbutane, within only six minutes. Clean formation of the fluorosilane related to the organosilicon hydride accompanies the reduction. The workup consists of quenching with solid potassium carbonate followed by addition of water, drying of the dichloromethane solution, and normal product isolation.¹²⁶



A variety of para-substituted 2-phenyl-2-butanols undergo quick and efficient reductions to the corresponding 2-phenylbutanes when they are dissolved in dichloromethane and a 2–10% excess of phenylmethylneopentylsilane and boron trifluoride is introduced at 0° (Eq. 30).¹²⁶ Several reactions deserve mention. For example, when $\text{R} = \text{CF}_3$, use of trifluoroacetic acid produces no hydrocarbon product, even after two hours of reaction time. In contrast, addition of boron trifluoride catalyst provides an 80% yield of product after only two minutes. When $\text{R} = \text{MeO}$, both trifluoroacetic acid and boron trifluoride produce a quantitative yield of the hydrocarbon within two minutes. However, when $\text{R} = \text{NO}_2$, attempts to promote the reduction with either trifluoroacetic acid or even methanesulfonic acid fail; even after reaction periods of up to eight hours, only recovered starting alcohol is obtained. Use of boron trifluoride provides a quantitative conversion into 2-(*p*-nitrophenyl)butane after only ten minutes. It is significant that the normally easily reducible nitro group survives these conditions entirely intact.^{126,129} Triethylsilane may be used as the silane.¹⁴³



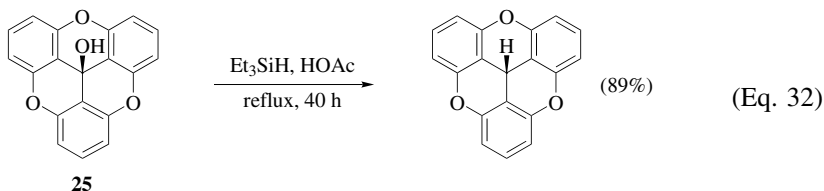
Treatment with triethylsilane and boron trifluoride etherate allows a variety of methyl β -hydroxy- β -arylpropionates to be reduced to methyl β -arylpropionates in yields of 85–100% as part of a synthetic sequence leading to the preparation of indanones (Eq. 31).¹⁷⁰ Small amounts of dehydration products formed simultaneously are reduced to the methyl β -arylpropionates by mild catalytic hydrogenation.¹⁷⁰



Diaryl and triaryl benzylic alcohols generally undergo smooth reduction to the corresponding hydrocarbons. Thus, both diphenyl- and triphenylcarbinol quickly give good to excellent yields of the corresponding substituted methanes when

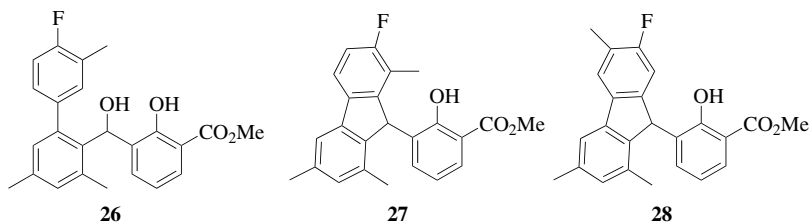
treated with triphenylsilane or Et_3SiH /trifluoroacetic acid in dichloromethane²⁶ or with triethylsilane and mixtures of either sulfuric or *p*-toluenesulfonic acids in acetic acid.¹³⁶ The reductions do not occur with the parent, unsubstituted carbinols using only acetic acid; however, tri-*p*-anisylcarbinol, 2,2',2'',6,6',6''-hexamethoxytriphenylcarbinol, 9-phenyl-9*H*-xanthen-9-ol, 9-*p*-anisyl-9*H*-xanthen-9-ol,²⁶ and 9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-9*H*-xanthen-9-ol²⁹ all undergo smooth conversion to the respective hydrocarbons when treated with acetic acid containing triethylsilane.

In fact, the use of acetic acid as both solvent and catalyst may be the method of choice in effecting the reductions of very electron-rich benzylic alcohols and those that form acid-labile reduction products. When 2,2',2'',6,6',6''-hexamethoxytriphenylcarbinol is treated with Et_3SiH /trifluoroacetic acid in dichloromethane, the reduction goes beyond the triarylmethane stage to produce one equivalent of 2,2',6,6'-tetramethoxydiphenylmethane and one equivalent of *m*-dimethoxybenzene.²⁶ These additional products are thought to arise from protonation of one of the electron-rich rings of the initially formed 2,2',2'',6,6',6''-hexamethoxytriphenylmethane at C1 by the trifluoroacetic acid. Expulsion of a molecule of *m*-dimethoxybenzene followed by hydride capture of the 2,6,2',6'-tetramethoxydiphenylmethyl "daughter" cation formed accounts for the final mixture of products.²⁶ Sesquixanthanol **25** undergoes reduction to the hydrocarbon only reluctantly, presumably because of the great stability of the sesquixanthyl cation (**1**). An early report indicates that the alcohol is able to resist reduction upon treatment with trifluoroacetic acid and excess triethylsilane in dichloromethane for 24 hours and to remain unreduced when dissolved in acetic acid containing triethylsilane.²⁶ A later report indicates formation of the hydrocarbon in 89% yield (Eq. 32).²⁹

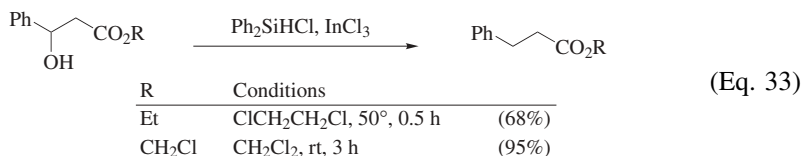


Intramolecular Friedel-Crafts reactions can sometimes compete with organosilicon hydride reductions of benzylic-type alcohols to cause formation of undesired products. An example is the attempted reduction of alcohol **26** to the corresponding hydrocarbon. When **26** is treated with triethylsilane in trifluoroacetic acid at room temperature for 15 hours, a mixture of the two fluorene isomers **27** and **28** is obtained in a combined yield of 45%. None of the hydrocarbon structurally related to the substrate alcohol **26** is obtained.¹⁷¹ Whether this problem could be circumvented by running the reduction at a lower temperature or with a different acid remains subject to experimentation.

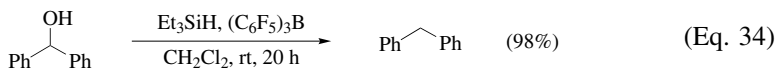
Both benzylic and secondary aliphatic alcohols are reduced with the combination of Ph_2ClSiH and a catalytic amount of indium trichloride. This combination



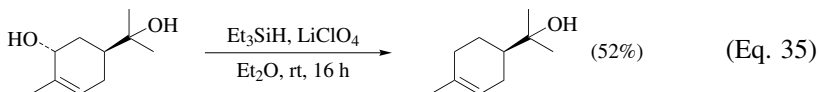
chemoselectively reduces benzyl alcohols in the presence of both ester and halide functions (Eq. 33).¹⁷²



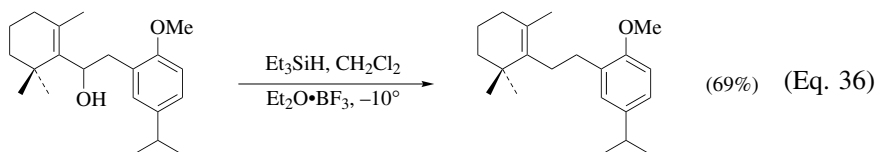
The combination of excess Et₃SiH and catalytic amounts (5–10 mol%) of (C₆F₅)₃B reduces benzylic alcohols to the hydrocarbons (Eq. 34), although the reaction stops at the non-reductive simple silylation of the alcohol with only a single equivalent of the silane.^{144,145}



Allyl Alcohols. Secondary cyclic allylic alcohols are reduced with the combination of Et₃SiH and ethereal LiClO₄, even in the presence of a tertiary alcohol (Eq. 35) or ketal function.¹⁷³ Primary allylic alcohols do not undergo deoxygenation under similar conditions.¹⁷³



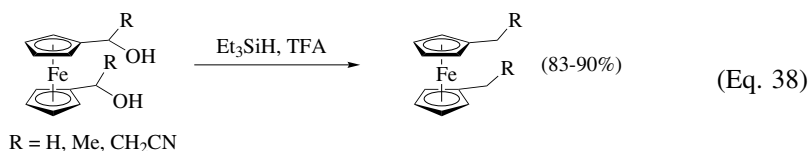
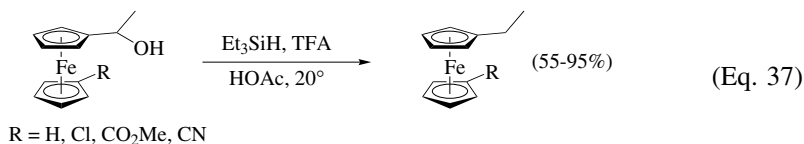
Treatment of 1-[2-(2-methoxy-5-isopropylphenyl)-1-hydroxyethyl]-2,6,6-trimethylcyclohexene with triethylsilane and boron trifluoride etherate in dichloromethane at –10° leads to its reduction to 2-(2,6,6-trimethyl-1-cyclohexenyl)-1-(2-methoxy-5-isopropylphenyl)ethane in 69% yield (Eq. 36).¹⁷⁴



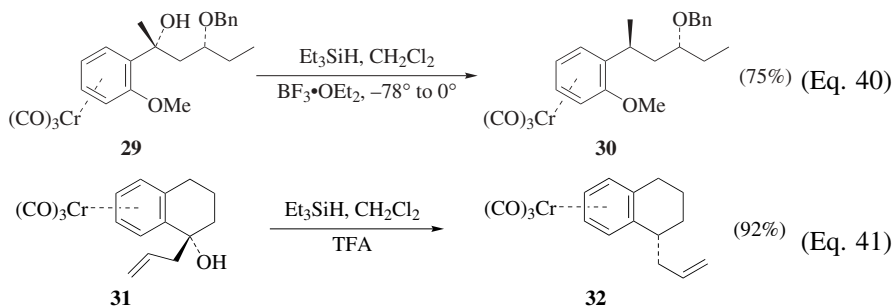
Metal-Complexed Alcohols. It is well known that carbocations are frequently stabilized when organotransition metal centers are present in adjacent portions of

the molecule.¹⁷⁵⁻¹⁷⁷ It is thus not surprising that alcohols possessing such centers are prone to undergo facile reduction upon treatment with acids and organosilicon hydrides. Perhaps it is more surprising that the coordinated metal centers survive the reduction conditions so well.

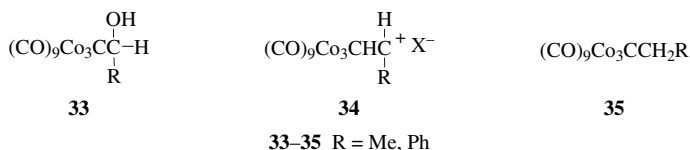
Methylferrocenylcarbinols bearing several functional groups ($R = H, Cl, CO_2Me, CN$) on the distal C_5 ring undergo reduction to the corresponding ethylferrocenes when treated with an excess of Et_3SiH/TFA in acetic acid solution at 20° (Eq. 37).¹⁷⁸ The yields of reduced product are no less than 85% within three hours, except when $R = CN$. Then the conversion into the ethylferrocene is only 55% complete after 20 hours of reaction time, reflecting the destabilizing effect of the cyano group on the intermediate carbocation. In a similar fashion, symmetrically disubstituted ferrocenylcarbinols undergo facile double deoxidative reduction in yields of more than 80% within three hours at 20° when dissolved in trifluoroacetic acid and treated with two equivalents of triethylsilane (Eq. 38).¹⁷⁹ The “half-sandwich” cyclopentadienylmanganese tricarbonyl (cymantrene) carbinol undergoes reduction in a similar way to that of its ferrocenylcarbinol analogs (Eq. 39).¹⁸⁰



Highly diastereoselective and chemoselective reductions may be performed on the hydroxy functions of $(\eta^6\text{-arene})\text{-tricarboxylchromium}$ complexes. Treatment of the chromium-complexed benzylic alcohol **29** with triethylsilane and boron trifluoride etherate in dichloromethane at -78° to 0° gives only diastereomer **30** in 75% yield (Eq. 40).¹⁸¹ In a similar fashion, treatment of the complexed exo-allyl-endo-benzylic alcohol **31** with an excess of Et_3SiH/TFA in dichloromethane at room temperature under nitrogen produces only the endo-allyl product **32** in 92% yield after 1.5 hours (Eq. 41). It is noteworthy that no reduction of the isolated double bond occurs.¹⁸²



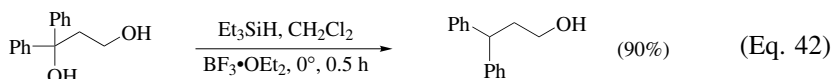
Treatment of α -hydroxyalkylidynetricobalt nonacarbonyl complexes of type **33** with strong acids produces the related highly stabilized carbocations **34**.¹⁸³ As expected, heating a tetrahydrofuran solution of the methyl compound (**33**, R = Me) with trifluoroacetic acid and triethylsilane at reflux for four hours produces the related hydrocarbon complex (**35**, R = Me) in 72% yield. Somewhat surprising, however, is the report that the hexafluorophosphate salt of the phenyl-substituted carbocation (**34**, R = Ph, $\text{X}^- = \text{PF}_6^-$), preformed by treatment of the corresponding alcohol with hexafluorophosphoric acid, produces only 7% of the related hydrocarbon complex when exposed to triethylsilane in tetrahydrofuran for 1.5 hours at room temperature. This lower yield of hydrocarbon complex from the phenyl system compared with the methyl analog is probably a reflection of the greater stability and lower reactivity of the intermediate cation.



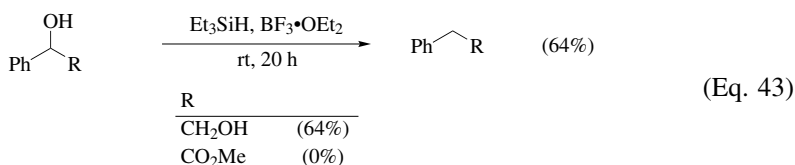
Polyfunctional Hydroxy Compounds. Different classes of alcohols can serve as the precursors to carbocations that have different stabilities and different degrees of ease of formation. It is thus no surprise that selective acid-catalyzed organosilicon hydride reductions of alcohols of one type may be effected in the presence of others if the proper reaction conditions are employed. For example, either tertiary or secondary benzylic hydroxy groups may be replaced by hydrogen without affecting primary aliphatic-type hydroxy groups in the same molecule when boron trifluoride etherate and triethylsilane are used.¹³⁷ This $\text{Et}_3\text{SiH}/\text{BF}_3 \cdot \text{OEt}_2$ reagent combination is also selective for a benzylic alcohol over an aliphatic alcohol function.¹³⁷

Treatment of 1,1-diphenylpropane-1,3-diol with two equivalents each of boron trifluoride etherate and triethylsilane in dichloromethane at 0° gives a 90% yield of 3,3-diphenylpropan-1-ol after 30 minutes (Eq. 42). Replacement of the terminal CH_2OH group by a CO_2Et group and similar treatment produces a product mixture containing 50% of the reduced product and 18% of the corresponding

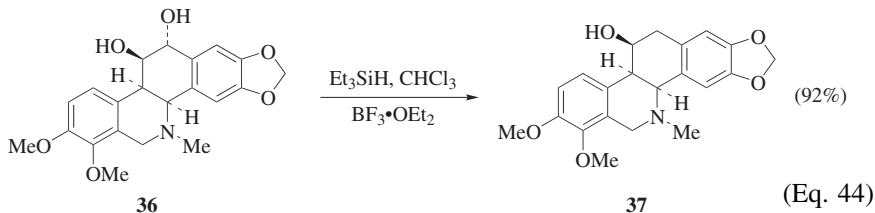
alkene elimination product. The carboethoxy group is unaffected by these reduction conditions.¹³⁷



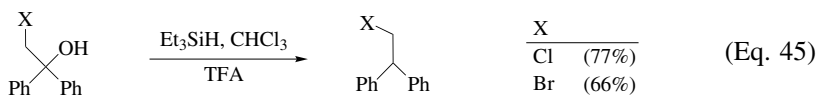
The secondary benzylic alcohol 1-phenylethan-1,2-diol requires 20 hours of treatment at room temperature to produce a 64% yield of 2-phenylethanol (Eq. 43).¹³⁷ Under the same conditions, methyl mandelate fails to undergo reduction, presumably because of the greater carbocation-destabilizing effect of a neighboring carboalkoxy compared to a hydroxymethyl group (Eq. 43).¹³⁷



Triethylsilane/boron trifluoride etherate in chloroform at room temperature reduces only the benzylic 12-hydroxy group of the polyfunctional compound **36** to form (±)-homochelidonine **37** in 92% yield (Eq. 44).¹³⁸



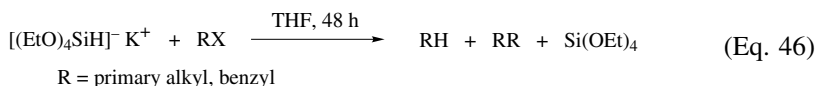
It is possible to effect reduction of tertiary benzylic hydroxy functions in the presence of primary halogens. Treatment of 1,1-diphenyl-1-hydroxy-2-haloethanes in chloroform with a slight excess of triethylsilane and a 9- to 10-fold excess of trifluoroacetic acid yields the corresponding 2,2-diphenyl-1-haloethanes (Eq. 45). The yield of the chloride is 77% after one hour at -15° , whereas that of the bromide is 66% following one hour at 0° .¹⁸⁴



Alkyl Halides and Triflates to Alkanes. The normal requirements for conversion of alkyl halides (and triflates) to alkanes using organosilicon hydrides are essentially the same as those needed for the reduction of the corresponding alcohols, namely, the substrates must generally be able to serve as precursors to

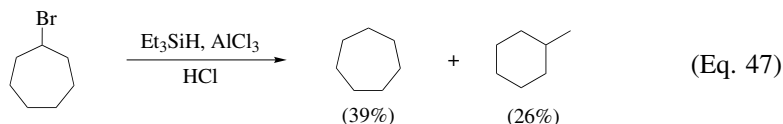
carbocations that may be captured by the hydride. The reduction of alkyl halides has been accomplished with triethylsilane/aluminum chloride. Substrates that undergo reduction under these conditions include primary alkyl halides,^{146,185,186} secondary alkyl halides,^{146,187,188} gem-dihalides,¹⁸⁹ vicinal dihalides,¹⁸⁹ and tertiary alkyl halides.^{187,188} As expected, haloarenes generally do not undergo such reductions, even under vigorous conditions.^{146,190}

An exception to the need for carbocation formation is found when the silyl hydride functional group is part of a valence-expanded hydrosilicate species. For example, potassium tetraethoxyhydrosilicate¹⁰⁴ is capable of reducing primary alkyl and benzylic bromides and chlorides directly to the corresponding hydrocarbons without the need for additional catalysis (Eq. 46).⁹⁵ The reaction is not a simple nucleophilic displacement of hydride for halide, however, since dimers can be formed as part of the reaction product mixture. In addition, when 6-bromo-1-hexene is used as the substrate, 4.4% of methylcyclopentane is obtained along with 63% of 1-hexene product.⁹⁵ The presence of the ring-closed product is suggestive of the operation of single-electron transfer (SET) processes.¹⁹¹



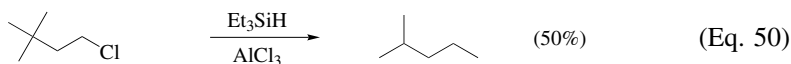
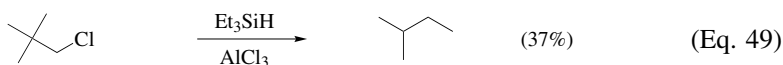
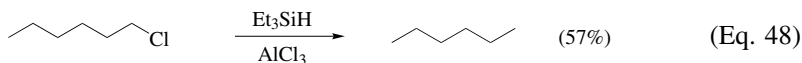
Alkyl Halides. Commonly, reductions with liquid silanes and liquid alkyl halides do not require the use of a solvent.¹⁸⁶ When the alkyl halide is a solid, either pentane¹⁸⁶ or dichloromethane may be used as solvent.¹⁹² No significant difference in reactivities is observed between alkyl chloride and bromide substrates,¹⁸⁶ but allyl halides are more reactive than 2-halopropanes, which, in turn, are more reactive than 1-halopropanes.^{190,146}

With halides having a strong propensity to undergo ionization, such as trityl halides, reductions may occur in the absence of added Lewis acids.^{29,54} Otherwise, the presence of Lewis acids is required. Catalytic amounts of aluminum bromide and aluminum chloride seem to be equally effective unless there are other Lewis base centers such as oxygen in the molecule to compete with the halogen for complexation with the Lewis acid.¹⁹² Then it is necessary to add more than one equivalent of the Lewis acid to effect reduction of the carbon-halogen function.^{136,146} Skeletal rearrangements may occur during these reductions, as in the reduction of bromocycloheptane (Eq. 47).^{146,185}

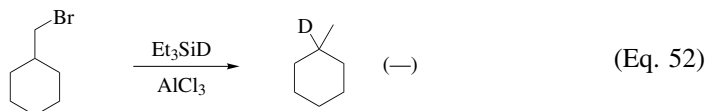
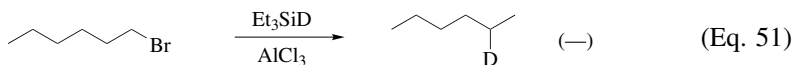


In contrast to the behavior of primary alcohols, which resist reduction by organosilicon hydrides even in the presence of very strong acids, primary haloalkanes, including methyl iodide and ethyl bromide,¹⁸⁶ undergo reduction when treated with aluminum chloride and organosilicon hydrides.^{146,185,186} Slow addition of a catalytic amount of aluminum chloride to a nearly equimolar

mixture of 1-chlorohexane and triethylsilane produces a vigorous reaction that, after 28 hours and simple distillation, gives a 57% yield of *n*-hexane and an 88% yield of chlorotriethylsilane (Eq. 48).¹⁸⁵ Similar treatment of 2,2-dimethyl-1-chloropropane gives 2-methylbutane in 37% yield (Eq. 49), whereas treatment of 3,3-dimethyl-1-chlorobutane gives a 50% yield of 2-methylbutane (Eq. 50).¹⁸⁵ Polymeric hydrocarbon by-products accompany the products of the latter two reactions. The structures of the products are clear evidence of the occurrence of 1,2-alkyl shifts leading to more stable carbocationic intermediates.

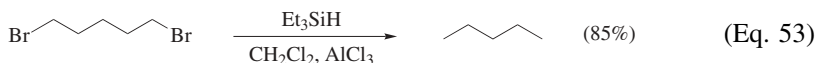


The use of a deuterium-labeled organosilicon hydride and location of the deuterium isotope in the reduced product shows that 1,2-hydride shifts also occur. Thus, reduction of 1-bromohexane with triethylsilane-*d*₁ yields hexane with all of the deuterium at C2 (Eq. 51); similar treatment of cyclohexylmethyl bromide produces methylcyclohexane-1-*d*₁ (Eq. 52).¹⁸⁶



Trialkylsilanes are generally more effective than dialkyl- or monoalkylsilanes in minimizing isomerizations. The reduction of 2-bromododecane to dodecane proceeds under aluminum chloride catalysis in 82% yield using *n*-butylsilane and in 87% yield with tri-*n*-butylsilane.¹⁸⁶ However, similar treatment of bromocycloheptane with triethylsilane yields a mixture of 39% cycloheptane and 26% methylcyclohexane. The same substrate yields 65% methylcyclohexane and less than 1% cycloheptane when *n*-butylsilane is the reducing agent.¹⁸⁶

Total reduction of unbranched open-chain and cyclic derivatives of dichloro and dibromo alkanes occurs at room temperature within 30 minutes in dichloromethane solutions containing ca. 2.5 equivalents of triethylsilane and ca. 0.25 equivalents of aluminum chloride.¹⁸⁹ The reaction occurs equally well with geminal, vicinal, and ω -dihalo alkanes. For example, 1,5-dibromopentane gives *n*-pentane in 85% yield when treated in this way (Eq. 53).¹⁸⁹

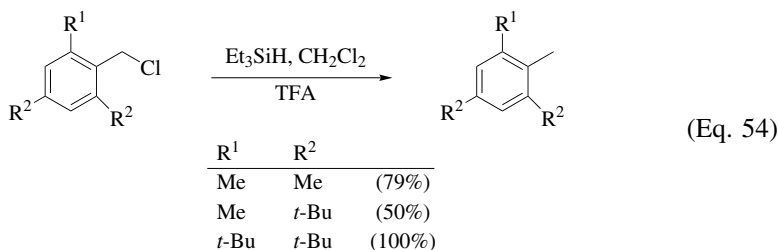


Chlorocyclohexane is converted into cyclohexane in dichloromethane using ethyldichlorosilane as reducing agent.¹⁹² The product yield is 40% with 25 mol% aluminum chloride and 45% with aluminum bromide. 1-Chloro-1-methylcyclohexane gives a 94% yield of methylcyclohexane using aluminum chloride and a 92% yield with aluminum bromide. Ethyldichlorosilane is superior as a hydride donor to either cumene or dicumylmethane.¹⁹²

2-Bromoadamantane and 1-bromoadamantane are reduced to adamantane in yields of 84% and 79%, respectively, when treated with triethylsilane and catalytic amounts of aluminum chloride.¹⁸⁶ Similar treatment of benzhydryl chloride and *exo*-2-bromonorbornane gives the related hydrocarbons in yields of 100% and 96%, respectively.¹⁸⁶ In contrast, 2-bromo-1-phenylpropane gives only a 43% yield of 1-phenylpropane; the remainder consists of Friedel-Crafts alkylation products.¹⁸⁶ Some alkyl halides resist reduction by this method, even when forcing conditions are employed. These include *p*-nitrobenzyl bromide, 3-bromopropanenitrile, and 5-bromopentanenitrile.¹⁸⁶

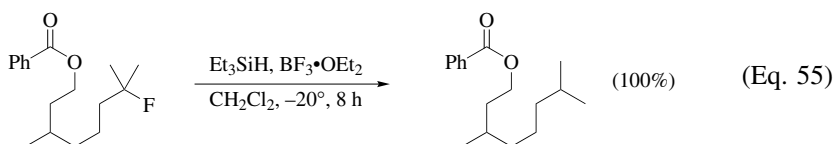
The reduction of 4-chloro-4-methyltetrahydropyran with triethylsilane requires more than a catalytic amount of aluminum chloride. No 4-methyltetrahydropyran is obtained after 20 hours at room temperature even when 0.75 equivalents of the catalyst is used, but a 92% yield is obtained after only 30 minutes when two equivalents of catalyst and three equivalents of triethylsilane are used.^{136,146} This is presumably a result of the ability of the Lewis acid to coordinate at the ring oxygen as well as at the chlorine. The introduction of alkyl groups at C2 appears to introduce enough steric hindrance near the ring oxygen to enable less than one equivalent of aluminum chloride to effect reduction, but also makes the products unstable to the reaction conditions so that the synthetic yields decline compared with the unsubstituted substrate.¹³⁶

Dichloromethane solutions of some sterically congested benzyl chlorides and triethylsilane need only the addition of excess trifluoroacetic acid to promote rapid conversion of the chlorides to the related hydrocarbons.¹²⁸ Thus 2,4,6-trimethylbenzyl chloride produces a 79% yield of isodurene at room temperature after 2.5 hours, 2-methyl-4,6-di-*tert*-butylbenzyl chloride gives 50% 1, 2-dimethyl-4,6-di-*tert*-butylbenzene after 40 minutes at reflux, and 2,4,6-*tert*-butylbenzyl chloride gives a 100% yield of 2,4,6-tri-*tert*-butyltoluene within 17 minutes at reflux (Eq. 54). The unsubstituted parent benzyl chloride remains unreacted under these conditions even after 30 days.¹²⁸

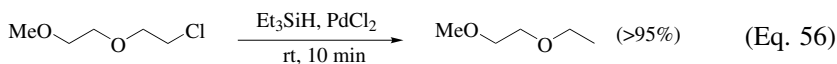


It is clear that the ionizing power of the solvent used is important in many of these reductions. When 2,4,6-trimethylbenzyl chloride is heated with diphenylsilane in nitrobenzene at temperatures as high as 130°, no isodurene is formed.¹⁹³ Not unexpectedly, the same lack of reactivity is reported for a series of benzyl fluorides, chlorides, and bromides substituted in the para position with nitro or methyl groups or hydrogen when they are heated in nitrobenzene solutions with triethylsilane, triethoxysilane, or diphenylsilane.¹⁹³

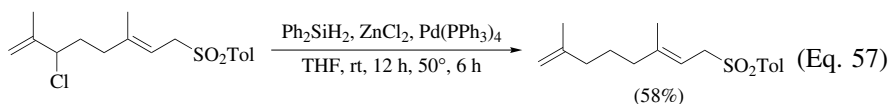
The combination of boron trifluoride etherate and triethylsilane can cause the reduction of tertiary fluoride centers even in polyfunctional compounds (Eq. 55).¹⁹⁴



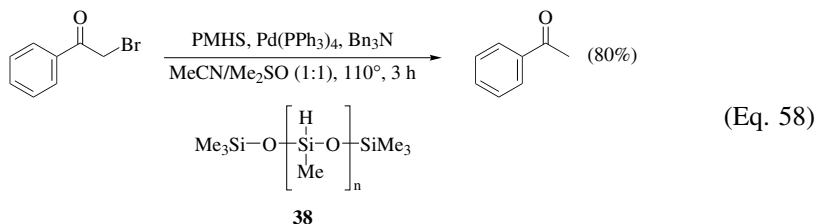
Alkyl iodides, benzyl chlorides, benzyl bromides, and adamantyl bromides and iodides undergo reduction with triethylsilane/palladium chloride.¹⁹⁵ The reduction of a β -chloro ether occurs in excellent yield with this system (Eq. 56).¹⁹⁵



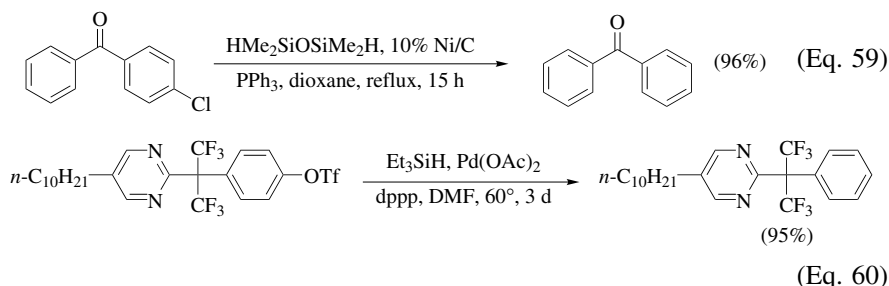
Allyl Halides. Reduction of a polyfunctional allyl chloride occurs without rearrangement and without reduction of the tosylate using $\text{Ph}_2\text{SiH}_2/\text{ZnCl}_2/\text{Pd}(\text{PPh}_3)_4$ (Eq. 57).¹⁹⁶



α -Halocarbonyl Compounds. The reduction of α -chloro and α -bromo ketones and esters has been accomplished with combinations of $\text{PhSiH}_3/\text{Mo}(\text{CO})_6$,¹⁹⁷ $\text{Ph}_2\text{SiH}_2/\text{ZnCl}_2/\text{Pd}(\text{PPh}_3)_4$,¹⁹⁷ $\text{Ph}_2\text{SiH}_2/\text{Pd}(\text{OAc})_2$,¹⁹⁷ and $\text{Et}_3\text{SiH}/\text{PdCl}_2$,¹⁹⁵ with the first reagent combination giving the best results.¹⁹⁷ One example of an α -chloro amide reduction is reported.¹⁹⁸ 2-Bromopropiophenone is reduced to propionic acid with polymethylhydrosiloxane (PMHS, **38**), an inexpensive industrial commodity, and $\text{Pd}(\text{PPh}_3)_4$ in 35% yield.¹⁹⁹ This reagent combination also reduces α -halo ketones in high yields (Eq. 58).¹⁹⁹



Vinyl and Aryl Halides and Triflates. The organosilane reduction of aryl halides is possible in high yields with triethylsilane and palladium chloride.¹⁹⁵ The reaction is equally successful with aryl chlorides, bromides, and iodides. Aryl bromides and iodides, but not chlorides, are reduced with PMHS/Pd(PPh₃)₄ in moderate to excellent yields.¹⁹⁹ This system also reduces vinyl bromides.¹⁹⁹ *p*-Chlorobenzophenone is reduced to benzophenone with *sym*-tetramethyldisiloxane and Ni/C in excellent yield (Eq. 59).²⁰⁰ There is a report of the organosilane reduction of aryl and vinyl triflates in very high yields with the combination of Et₃SiH/Pd(OAc)₂/dppp (1,3-bis(diphenylphosphino)propane) (Eq. 60).²⁰¹



Reduction of Unsaturated Hydrocarbons

Alkenes to Alkanes. The “ionic hydrogenation” of many compounds containing carbon-carbon double bonds is effected with the aid of strong acids and organosilicon hydrides following the π -route outlined in Eq. 2. A number of factors are important to the successful application of this method. These include the degree and type of substituents located around the double bond as well as the nature and concentrations of the acid and the organosilicon hydride and the reaction conditions that are employed.

The most common reaction conditions for alkene reductions use excess trifluoroacetic acid and triethylsilane either neat^{202–204} or in an inert solvent such as nitrobenzene,¹³⁴ 2-nitropropane,²⁰⁵ carbon tetrachloride,²⁰⁶ chloroform,²⁰⁷ or dichloromethane.^{127,164} Reaction temperatures from -78° to well over 100° are reported. Ambient or ice-bath temperatures are most commonly used, but variations of these conditions abound.

Among other silicon hydrides reported are *n*-butylsilane, diethylsilane, triisopentylsilane, tricyclopentylsilane, triphenylsilane, tri-*sec*-butylsilane, di-*tert*-butylsilane, di-*tert*-butylmethylsilane, tri-*tert*-butylsilane,²⁰⁴ phenylsilane, diethylmethylsilane,²⁰² diphenylsilane,^{134,208,209} dichloroethylsilane,¹⁹² PMHS,⁷⁷ and polyethylhydrosiloxane.²⁰⁷

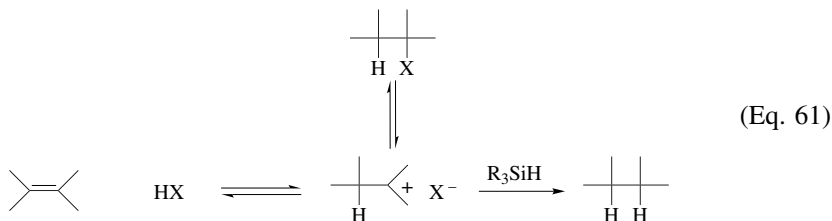
Acids that are used in addition to trifluoroacetic acid include trifluoroacetic acid with added sulfuric acid²⁰³ or boron trifluoride etherate,^{210,211} perfluorobutyric acid,²¹² hydrogen chloride/aluminum chloride,^{136,146,213} perchloric acid in chloroform,²¹⁴ *p*-toluenesulfonic acid alone¹³⁴ or with aluminum bromide or aluminum chloride,¹⁹² concentrated sulfuric acid in two-phase systems with dichloromethane, alcohol, or ether solvents,^{209,215} trifluoromethanesulfonic acid,²¹⁶ chlorodifluoroacetic acid,¹³⁴ and the monohydrate of boron trifluoride

($\text{BF}_3 \cdot \text{OH}_2$).²¹⁷ The use of a sulfonated phenol-formaldehyde polymer in conjunction with formic acid is also reported.²⁰⁸ Acids that are ineffective include phosphoric,²⁰⁸ trichloroacetic, dichloroacetic, and acetic acids.¹³⁴ It is reported that addition of lithium perchlorate to the reaction mixture improves product yields.^{193,205}

Other organosilane/acid reagent combinations that are used in the reduction of olefins to alkanes include $\text{Et}_3\text{SiH}/\text{NH}_4\text{F}/\text{TFA}$,¹³⁵ $\text{Et}_3\text{SiH}/\text{HClO}_4$,²¹⁴ $\text{Et}_3\text{SiH}/\text{TiCl}_4$,²¹⁸ PMHS/Pd-nanocomposite,²¹⁹ $\text{Et}_3\text{SiH}/\text{TFA}/\text{HClO}_4$,²⁰⁵ $\text{Et}_3\text{SiH}/\text{PdCl}_2$,²²⁰ polyethylhydrogensiloxane (PEHS)/TFA,²⁰⁷ $\text{Et}_3\text{SiH}/\text{TMSOTf}$,²¹⁶ and $\text{Et}_3\text{SiH}/\text{HCO}_2\text{H}$.²⁰⁸

The triethylsilane/trifluoroacetic acid reagent system reduces alkenes to alkanes in poor to excellent yields depending largely on the ability of the alkene to form carbocations upon protonation. Under these conditions the more substituted olefins are reduced in better yields and styrene double bonds are reduced in high yields.^{127,202,207,221–228} The reduction of 1,2-dimethylcyclohexene with this reagent gives a mixture of *cis*- and *trans*-1,2-dimethylcyclohexane.²²⁹ The formation of the trifluoroacetate esters is a side reaction.^{205,230}

Potential problems associated with double bond reduction by this method may be understood in terms of Eq. 61. Protonation of the double bond leads to the formation of the more stable carbocation. This carbocation may rearrange by a first-order process or react competitively with either indigenous nucleophiles or added silicon hydride by second-order processes. If strong nucleophiles such as those associated with weak Brønsted acids are present, then the limited degree of reversibility of carbocation regeneration following nucleophilic capture may lead to diversion of the desired reduction products to unwanted nucleophilic substitution products.²⁰⁹ Another problem exists if bimolecular polymerization reactions compete with carbocation capture by organosilicon hydrides because of the proximity of carbocations and unprotonated alkene substrate. When this occurs, yields of reduced product suffer. The yields of hydrocarbons from alkenes are, in fact, frequently lower than those of the same products derived from the corresponding alcohols because of this problem.^{134,142}



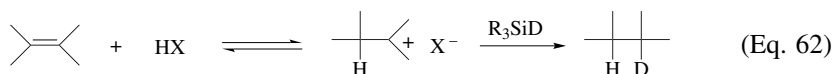
When trifluoroacetic acid is used as the source of protons, it is known that rapid formation of trifluoroacetate esters precedes reduction to hydrocarbons.^{134,204,206} Use of acetic acid in place of trifluoroacetic acid, for example, would be expected to fail to produce good conversion to reduced product because of the combination of decreased acidity and increased nucleophilicity of acetic acid relative to

trifluoroacetic acid as well as its weaker ionizing power as a solvent. This is consistent with experimental observations.^{134,209}

The relative stability of the carbenium ion resulting from double bond protonation is a controlling factor in the limitation of this method of hydrogenation. On a practical level, only alkenes that can produce carbenium ions at least as stable as tertiary aliphatic ones undergo reduction to alkanes in useful yields. This distinction serves as a basis for selectivity of reduction. Under essentially every set of conditions reported, 1-methylcyclohexene, which forms a tertiary aliphatic carbenium ion upon protonation, undergoes reduction to methylcyclohexane in good to excellent yields, whereas cyclohexene, which can only form a secondary aliphatic carbenium ion intermediate upon protonation, does not normally undergo reduction. Indeed, treatment of an equimolar mixture of cyclohexene and 1-methylcyclohexene with two equivalents of triethylsilane and four equivalents of trifluoroacetic acid at 50° gives, after 10 hours, a 70% yield of methylcyclohexane together with completely recovered, unreacted cyclohexene.²³¹

An exception is reported when the reactions are conducted using a two-fold excess of dichloroethylsilane with equal equivalents of either aluminum chloride or aluminum bromide and *p*-toluenesulfonic acid at 40° for two hours in dichloromethane. Under these conditions, 1-methylcyclohexene affords methylcyclohexane in 65–75% yield, whereas cyclohexene gives cyclohexane in 17–23% yield.¹⁹²

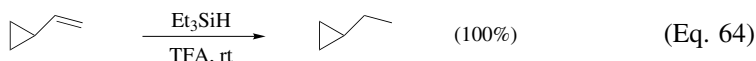
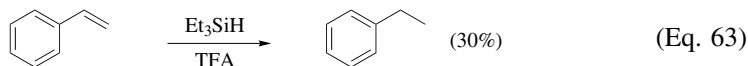
The use of deuterated organosilicon hydrides in conjunction with proton acids permits the synthesis of site-specific deuterium-labeled compounds.^{59,126,221} Under such conditions, the deuterium atom in the final product is located at the charge center of the ultimate carbocation intermediate (Eq. 62). With the proper choice of a deuterated acid and organosilicon hydride, it may be possible to use ionic hydrogenation in a versatile manner to give products with a single deuterium at either carbon of the original double bond, or with deuterium atoms at both carbon centers.¹²⁷



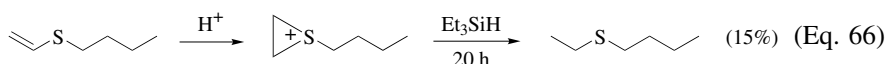
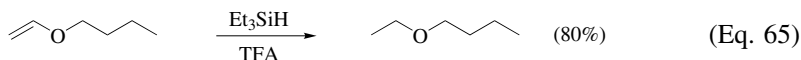
Monosubstituted Alkenes. Simple unbranched terminal alkenes that have only alkyl substituents, such as 1-hexene,²⁰³ 1-octene,²⁰⁹ or allylcyclohexane²³⁰ do not undergo reduction in the presence of organosilicon hydrides and strong acids, even under extreme conditions.^{1,2} For example, when 1-hexene is heated in a sealed ampoule at 140° for 10 hours with triethylsilane and excess trifluoroacetic acid, only a trace of hexane is detected.²⁰³ A somewhat surprising exception to this pattern is the formation of ethylcyclohexane in 20% yield upon treatment of vinylcyclohexane with trifluoroacetic acid and triethylsilane.²³⁰ Protonation of the terminal carbon is thought to initiate a 1,2-hydride shift that leads to the formation of the tertiary 1-ethyl-1-cyclohexyl cation.²³⁰

On the other hand, if the single substituent can stabilize an adjacent carbocation center following protonation of the alkene, then reduction may occur.

Styrene is reported to undergo reduction upon treatment with trifluoroacetic acid and triethylsilane,²⁰³ although competing polymerization reactions limit the yield of ethylbenzene to only 30% (Eq. 63).⁷⁰ Vinylcyclopropane is reduced to ethylcyclopropane within 30 minutes under similar conditions (Eq. 64).²³² It is important to note that the cyclopropane ring of ethylcyclopropane can be opened under these reaction conditions, albeit with longer reaction times, to give some *trans*-2-pentene in the final reaction mixture.²³³

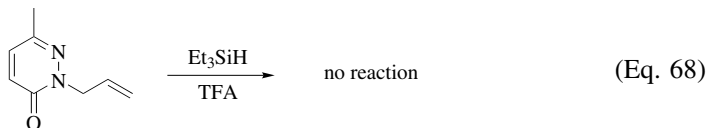
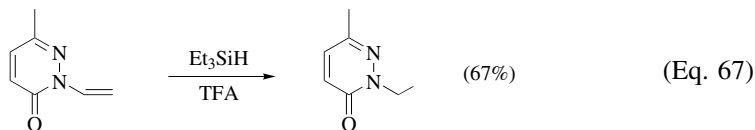


Examples of the behavior of other substituted vinyl substrates upon exposure to the action of trifluoroacetic acid and triethylsilane are known. For example, *n*-butyl vinyl ether, when reacted at 50° for 10 hours, gives *n*-butyl ethyl ether in 80% yield (Eq. 65).²³⁴ In contrast, *n*-butyl vinyl thioether gives only a 5% yield of *n*-butyl ethyl sulfide product after 2 hours and 15% after 20 hours of reaction.²³⁴ It is suggested that this low reactivity is the result of the formation of a very stable sulfur-bridged carbocation intermediate that resists attack by the organosilicon hydride (Eq. 66).



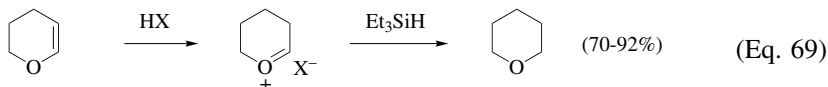
Attempted reduction of vinyl acetate yields a mixture containing 8% ethyl acetate and 3% ethyl trifluoroacetate after 10 hours. The amounts of the two esters change to 13% and 12%, respectively, at reaction times beyond 60 hours.²³⁴ Vinyl trifluoroacetate does not undergo reduction under these conditions, even after 75 hours.²³⁴

Treatment of *N*-vinyl-3-methyl-6-pyridazone with excess trifluoroacetic acid and triethylsilane at 65° for 25 hours yields 67% of the reduced product *N*-ethyl-3-methyl-6-pyridazone (Eq. 67).²³⁵ It is noteworthy that only the vinyl group in this compound undergoes reduction under these conditions, and not the ring or carbonyl sites. Examination of a solution of the starting *N*-vinyl-3-methyl-6-pyridazone in neat trifluoroacetic acid by ¹H NMR spectroscopy shows the existence of the trifluoroacetate ester expected from the carbocation formed by protonation of the vinyl group at the terminal carbon. It is of interest that a similar compound, *N*-allyl-3-methyl-6-pyridazone, is inert under these conditions (Eq. 68). This reflects the differences of the relative stabilities of the carbocations formed upon protonation of the C=C groups in each reaction.



Disubstituted Alkenes. Simple 1,2-disubstituted alkenes such as 2-octene or cyclohexene, which produce only secondary aliphatic carbocation reaction intermediates, do not undergo reduction upon treatment with a Brønsted acid and an organosilicon hydride. Even when extreme conditions are employed, only traces of reduction products are detected.^{192,203,207–210,214} An exception is the report that 4-methyl-2-pentene forms 2-methylpentane in 70% yield when heated to 50° for 20 hours with a mixture of Et₃SiH/TFA containing a catalytic amount of sulfuric acid. It is believed that 4-methyl-2-pentene is isomerized to 2-methyl-2-pentene prior to reduction.²⁰³

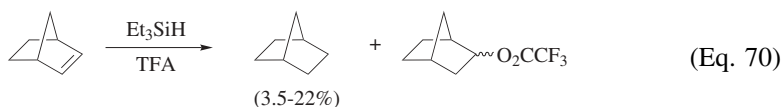
Unlike cyclohexene, its oxa analog, 3,4-dihydro-2*H*-pyran, undergoes facile reduction to tetrahydropyran in yields ranging from 70 to 92% when treated with a slight excess of triethylsilane and an excess of either trifluoroacetic acid or a combination of hydrogen chloride and aluminum chloride (Eq. 69).¹⁴⁶ This difference in behavior can be understood in terms of the accessibility of the resonance-stabilized oxonium ion intermediate formed upon protonation.



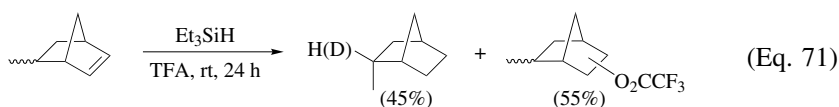
The behavior of the isomeric dihydronaphthalenes emphasizes the importance of the relative stabilities of carbocation intermediates in ionic hydrogenations. Treatment of 1,2-dihydronaphthalene with Et₃SiH/TFA at 50–60° gives a 90% yield of tetralin after one hour. Under the same conditions, the 1,4-dihydronaphthalene isomer gives less than 5% of tetralin after 70 hours.²²⁴ This difference in reactivity is clearly related to the relatively accessible benzylic cation formed upon protonation of the 1,2-isomer compared to the less stable secondary cation formed from the 1,4-isomer.²²⁴

The behavior of members of the bicyclo[2.2.1]heptene family is also different from that of other common 1,2-disubstituted alkenes.²³⁰ The parent bicyclo[2.2.1]heptene gives bicyclo[2.2.1]heptane in only 3.5% yield when it is treated with Et₃SiH/TFA. The major product is reported to be a 2-bicyclo[2.2.1]heptyl trifluoroacetate of unspecified configuration (Eq. 70).²³⁰ The carbocation intermediate is presumably the 2-norbornyl cation. Addition of small amounts of boron trifluoride etherate to the reaction mixture causes the yield of hydrocarbon product to rise to 22% after a reaction time of 24 hours at room temperature. Further

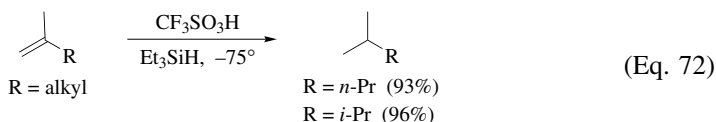
exposure of the reaction mixture to the reaction conditions does not result in additional hydrocarbon formation from the ester.



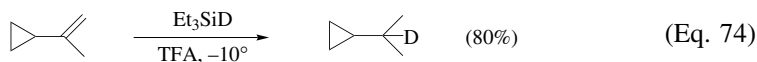
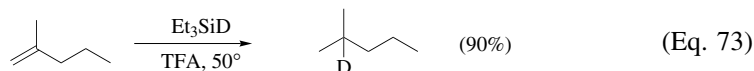
A mixture of *exo*- and *endo*-isomers of 5-methylbicyclo[2.2.1]hept-2-ene is hydrogenated with the aid of five equivalents of triethylsilane and 13.1 equivalents of trifluoroacetic acid to produce a 45% yield of *endo*-2-methylbicyclo[2.2.1]heptane (Eq. 71). The same product is formed in 37% yield after only five minutes. The remainder of the reaction products is a mixture of three isomeric secondary *exo*-methylbicyclo[2.2.1]heptyl trifluoroacetates that remains inert to the reaction conditions. Use of triethylsilane-1-*d*₁ gives the *endo*-2-methylbicyclo[2.2.1]heptane product with an *exo*-deuterium at the tertiary carbon position shared with the methyl group. This result reflects the nature of the internal carbocation rearrangements that precede capture by the silane.²³⁰



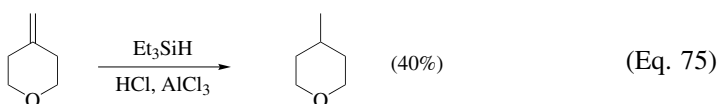
Alkenes with a 1,1-disubstitution pattern form tertiary carbocations upon treatment with a Brønsted acid. Consequently, such compounds are often easily reduced (Eq. 72). An example of this is the formation of 2-methylpentane in 93% yield after only 5 minutes when a dichloromethane solution of 2-methyl-1-pentene and 1.4 equivalents of triethylsilane is treated with 1.4 equivalents of trifluoromethanesulfonic acid at -75° .²¹⁶ Similar treatment of 2,3-dimethyl-1-butene gives a 96% yield of 2,3-dimethylbutane.²¹⁶



Use of deuterated silane and/or acid with this method leads to site-specific deuterium incorporation in the reduced products. Thus, treatment of 2-methyl-1-pentene with one equivalent of deuterated triethylsilane and two equivalents of trifluoroacetic acid at 50° for 24 hours gives 2-methylpentane-2-*d*₁ in 90% yield (Eq. 73).²²¹ In the same way, isopropenylcyclopropane gives an 80% yield of deuterated isopropylcyclopropane after 30 minutes at -10° (Eq. 74).²²¹



Preferential protonation of oxygen in comparison to carbon prevents 4-methylenetetrahydropyran from undergoing reduction to 4-methyltetrahydropyran even when held at 70° for 10 hours in the presence of triethylsilane and a 20-fold excess of trifluoroacetic acid.¹⁴⁶ However, when the reaction conditions are changed so that a dichloromethane solution of the same substrate is treated with a mixture of four equivalents of triethylsilane and three equivalents of aluminum chloride in the presence of excess hydrogen chloride, a 40% yield of 4-methyltetrahydropyran product is obtained at room temperature after one hour (Eq. 75).¹³⁶

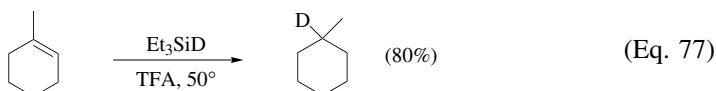


The cis-to-trans ratios of the isomeric 4-*tert*-butyl-1-methylcyclohexanes derived from treatment of 4-*tert*-butyl-1-methylenecyclohexane with trifluoroacetic acid vary with the steric features of the organosilicon hydrides that are used (Eq. 76).²⁰⁴ The ratio is 0.04 with *n*-butylsilane, 0.09 with diethylsilane, 0.11 with triethylsilane, 0.10 with triisopentylsilane, and 0.19 with either tri-*sec*-butylsilane or di-*tert*-butylsilane.



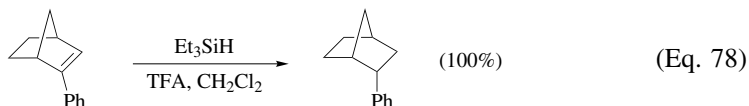
Trisubstituted Alkenes. With very few exceptions, trisubstituted alkenes that are exposed to Brønsted acids and organosilicon hydrides rapidly undergo ionic hydrogenations to give reduced products in high yields. This is best illustrated by the broad variety of reaction conditions under which the benchmark compound 1-methylcyclohexene is reduced to methylcyclohexane.^{134, 146, 192, 202, 203, 207–210, 214, 234}

When 1-methylcyclohexene is reduced with one equivalent of deuterated triethylsilane and two equivalents of trifluoroacetic acid at 50°, methylcyclohexane-1-*d*₁ is obtained in 80% yield after 24 hours (Eq. 77).²²¹ Under similar conditions, 2-methyl-2-butene gives 2-methylbutane-2-*d*₁ (90%) and 1-methylcyclopentene gives methylcyclopentane-1-*d*₁ (60%).²²¹

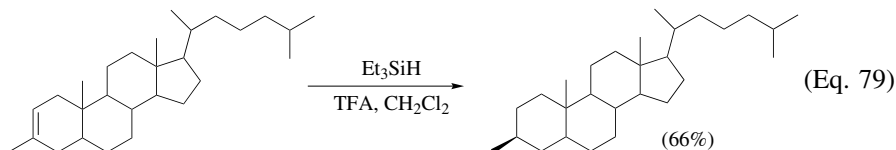


Surprisingly, α -cyanoacrylic acid is reported to react spontaneously with triethylsilane in the absence of any additional acid to give a quantitative yield of the triethylsilyl ester of α -cyanopropionic acid.²³⁶ Ethyl α -cyanoacrylate requires the presence of trifluoroacetic acid to undergo reduction to ethyl 2-cyanopropionate.²³⁶ Many of these reductions are highly stereoselective. For example, treatment of

2-phenylnorbornene with a solution of trifluoroacetic acid and triethylsilane in dichloromethane is reported to yield only *endo*-2-phenylnorbornane (Eq. 78).¹⁶⁴

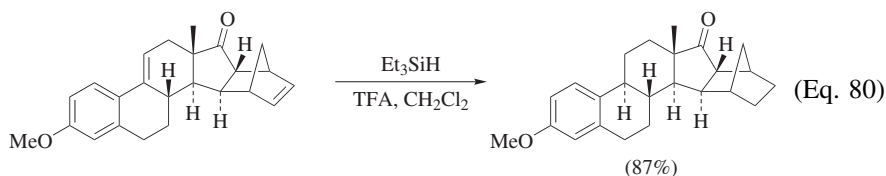


A mixture of Et_3SiH /TFA in dichloromethane reduces 3-methyl-5- α -cholest-2-ene to give the pure equatorial methyl isomeric product, 3 β -methyl-5 α -cholestane, in 66% yield (Eq. 79).¹²⁶ On the other hand, attempts to reduce cholest-5-ene using the same technique yield neither 5 α -cholestane nor 5 β -cholestane, but instead an isomeric mixture of rearranged olefins. This result is presumably because of the inability of hydride attack to compete with carbocation skeletal isomerization and elimination.¹²⁶

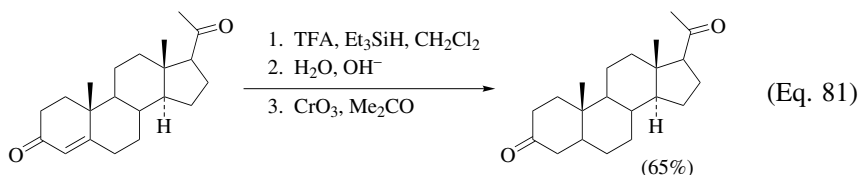


Treatment with trifluoroacetic acid and triethylsilane causes octahydro-6,7,8,12,13,14,16,17-15*H*-cyclopenta[*a*]phenanthrene to form decahydro-6,7,8,9,11,12,13,14,16,17-15*H*-cyclopenta[*a*]phenanthrene by reduction of the conjugated double bond.²³⁷ Similar treatment of the 3-methyl ether of $\Delta^{9(11)}$ -dehydro-D-homoe-*estrol* gives the 3-methyl ether of estradiol in better than 50% yield.²²⁶

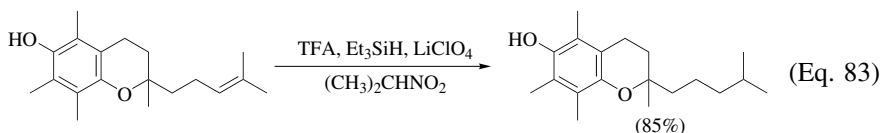
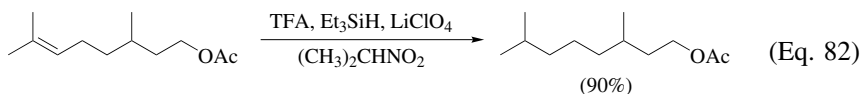
A similar transformation occurs as a critical step in the total synthesis of (+)-estrone by a Diels-Alder cycloaddition-cycloreversion pathway (Eq. 80).²²⁷ It is worth noting that in this reaction the conjugated double bond is stereoselectively reduced while both an isolated double bond and a ketone carbonyl are preserved.



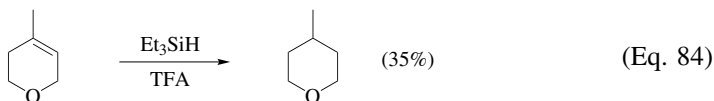
Treatment of progesterone with trifluoroacetic acid and triethylsilane in dichloromethane followed by saponification of the mixture of the trifluoroacetate ester intermediates of 5- β -pregnane-3 α ,20 β -diol and 5- β -pregnane-3 α ,20 α -diol and Jones oxidation yields 5- β -pregnanedione in 65% yield (Eq. 81).²³⁸



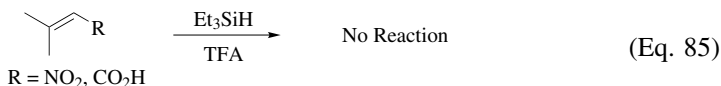
Hydrogenation of the carbon-carbon double bond occurs without alteration of the ester function when citronellyl acetate is treated with 2.5 equivalents of trifluoroacetic acid and two equivalents of triethylsilane in 2-nitropropane.²⁰⁵ The reduced product is obtained in 90% yield after 22 hours at room temperature in the presence of one equivalent of added lithium perchlorate (Eq. 82). The yields are lower in the absence of this added salt. Similar reduction of an unsaturated phenolic chroman derivative occurs to give an 85% yield of product with only the carbon-carbon double bond reduced (Eq. 83).²⁰⁵



A dichloromethane solution of 4-methyl-5,6-dihydro-2*H*-pyran gives 4-methyltetrahydropyran in 35% yield when treated with a mixture of five equivalents of triethylsilane and 2.5 equivalents of aluminum chloride in the presence of excess hydrogen chloride at room temperature for one hour (Eq. 84).¹³⁶ This behavior is essentially the same as that exhibited by the disubstituted 4-methylenetetrahydropyran isomer under similar conditions.¹³⁶



Exceptions to the generally facile ionic hydrogenation of trisubstituted alkenes include the resistance of both 2-methyl-1-nitropropene ($\text{R} = \text{NO}_2$) and 3,3-dimethylacrylic acid ($\text{R} = \text{CO}_2\text{H}$) to the action of a mixture of triethylsilane and excess trifluoroacetic acid at 50° (Eq. 85).²³⁴ The failure to undergo reduction is clearly related to the unfavorable effects caused by the electron-withdrawing substituents on the energies of the required carbocation intermediates.



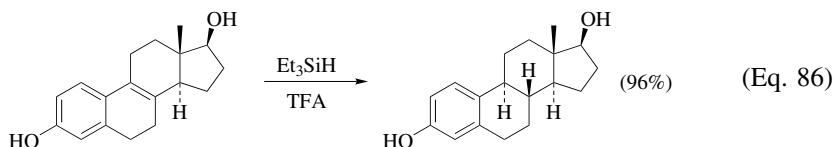
Tetrasubstituted Alkenes. Tetrasubstituted alkenes lacking electron-withdrawing substituents undergo facile ionic hydrogenation to alkanes in very good yields. Simple examples include 2,3-dimethyl-2-butene,^{208,214} 1,2-dimethylcyclopentene,²²⁹ and $\Delta^{9(10)}$ -octalin.^{126,204,212}

Interesting variations are observed in the stereoselectivities of these ionic hydrogenations. Reduction of 1,2-dimethylcyclopentene with $\text{Et}_3\text{SiH/TFA}$ near

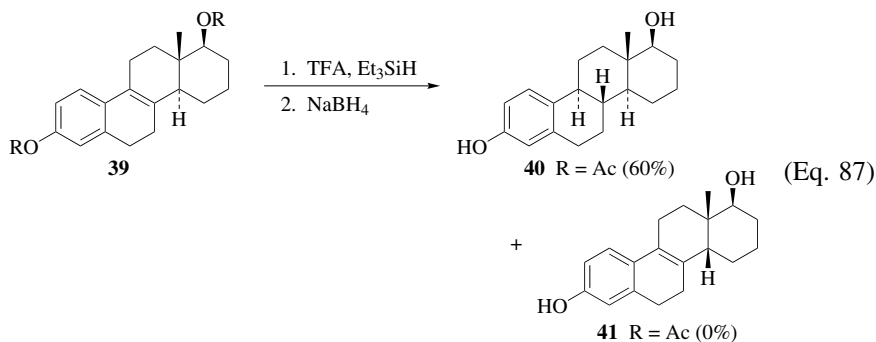
room temperature gives 1,2-dimethylcyclopentane with a *cis* to *trans* ratio of 0.083, compared to a ratio of 0.63 for 1,2-dimethylcyclohexene.²²⁹

The reduction of $\Delta^{9(10)}$ -octalin to *cis*- and *trans*-decalins occurs with *cis* to *trans* stereoselectivities that vary with the nature of the organosilicon hydride employed. The ratios are 0.28–0.59 with *n*-butylsilane, 0.67 with diethylsilane,²⁰⁴ 0.34²¹² or 0.72²⁰⁴ with triethylsilane, 0.67 with diphenylsilane, 0.77 with diphenylmethylsilane,²¹² 1.38²⁰⁴–1.80^{127,212} with triphenylsilane, 0.54 with triisopentylsilane, 1.17 with tricyclopentylsilane, 2.57 with tri-*sec*-butylsilane, 3.35 with di-*tert*-butylsilane, 4.88 with di-*tert*-butylmethylsilane, and 13.3 with tri-*tert*-butylsilane.²⁰⁴ Opinions differ about the mechanistic significance of these changes in isomer ratios.^{204,212}

Treatment of $\Delta^{8(9)}$ -dehydroestradiol with trifluoroacetic acid and triethylsilane gives estradiol in 96% yield (Eq. 86).²³⁹ The 3-methyl ether is similarly reduced to the 3-methyl ether of estradiol in >50% yield.²³⁹ The structurally related 18-ethyl and 18-propyl 17-keto compounds experience reduction of the $\Delta^{8(9)}$ function in excess of 70% yield without concomitant reduction of the 17-keto group.²³⁹



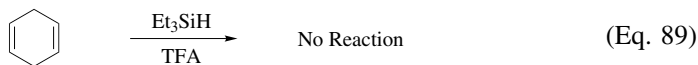
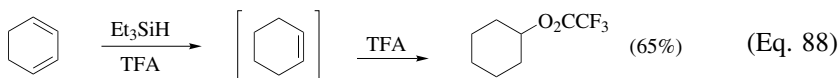
Treatment of $\Delta^{8(9)}$ -dehydro-D-homoestradiol (**39**, R = H) (or its 3-methyl ether, R = Me) with Et₃SiH/TFA followed by saponification of the trifluoroacetate ester intermediate leads to D-homoestradiol (**40**) (or its 3-methyl ether) containing 2–15% D-homoequilenol (**41**) (or its 3-methyl ether).²⁴⁰ By contrast, reduction and saponification of 3,17-diacetyl- $\Delta^{8(9)}$ -dehydro-D-homoestradiol (**39**, R = AcO) gives a 60% yield of D-homoestradiol without the presence of any D-homoequilenol (Eq. 87).²⁴⁰



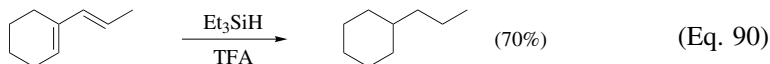
Polyenes. The behavior of substrates with multiple carbon-carbon double bonds toward the conditions employed for ionic hydrogenations with organosilicon hydrides depends heavily on the number and kinds of substituents and

whether or not the multiple double bonds are conjugated. In the absence of conjugation, the individual double bonds react independently.

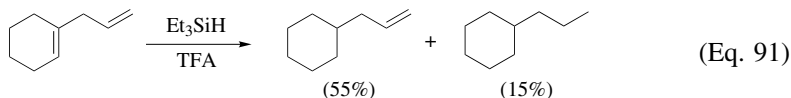
The full reduction of 1,3-dienes with $\text{Et}_3\text{SiH/TFA}$ occurs in certain systems although the yields are only modest.²³¹ For example, 1,3-cyclohexadiene gives a 65% yield of cyclohexyl trifluoroacetate, presumably by way of cyclohexene (Eq. 88).²¹¹ On the contrary, 1,4-cyclohexadiene fails to undergo reaction with 10 equivalents of triethylsilane and 20 equivalents of trifluoroacetic acid even after 24 hours at room temperature (Eq. 89).



Additional evidence of this pattern of behavior is shown upon treatment of the conjugated diene 1-propenylcyclohexene with two equivalents of triethylsilane and three equivalents of trifluoroacetic acid at 50° . This diene gives a 70% yield of completely reduced propylcyclohexane after 10 hours (Eq. 90).²³¹ No partially reduced intermediates are found.

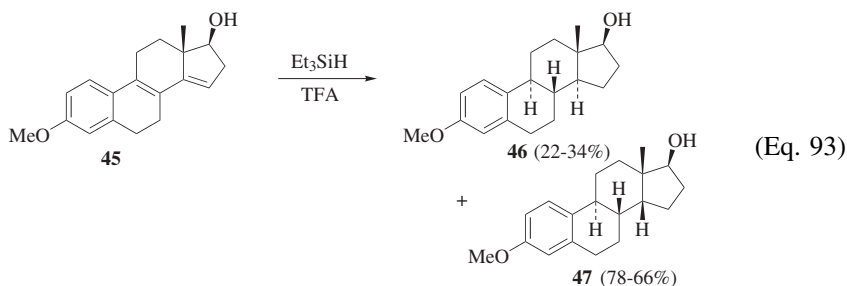
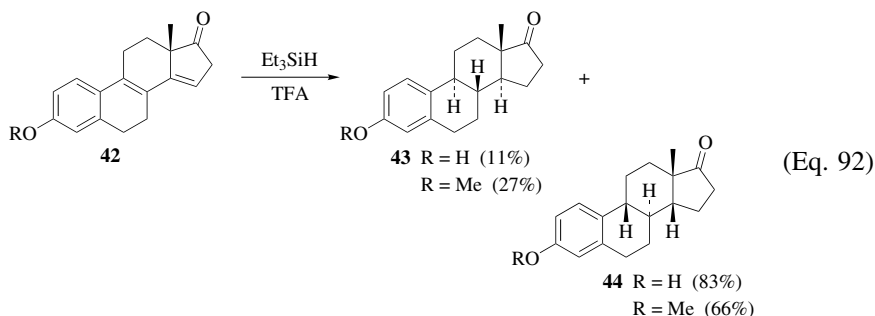


Similar treatment of the isomeric, nonconjugated 1-(3-propenyl)cyclohexene gives a mixture of products containing 55% of the partially reduced 3-propenylcyclohexene and 15% of the completely reduced propylcyclohexane (Eq. 91).²³¹ The yield of the latter product increases to 25% when the amounts of $\text{Et}_3\text{SiH/TFA}$ used are raised to 6.5 and 12.1 equivalents, respectively, and the reaction time is increased to 24 hours.²³⁰ The nonconjugated 1-(3-butenyl)cyclohexene gives a 65% yield of partially hydrogenated 3-butenylcyclohexene under identical conditions.²³¹

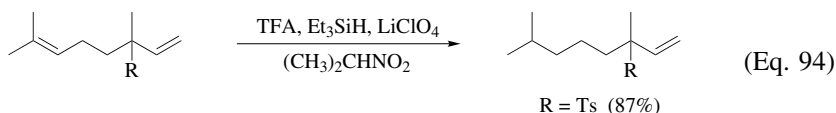


Reduction of dienes incorporated into steroid structures may lead to different configurations in the products. For example, treatment of 8(9),14(15)-bisdehydroestrone **42** ($\text{R} = \text{H}$) for four hours at room temperature with twenty equivalents of trifluoroacetic acid and two equivalents of triethylsilane leads to an ionic hydrogenation product mixture containing the natural $8\beta,9\alpha,14\alpha$ -estrone **43** as a minor component (11%) and the $8\alpha,9\beta,14\beta$ -isomer **44** as the major component (83%) (Eq. 92).²⁴¹ The related methyl ether (**42**, $\text{R} = \text{Me}$) behaves in a similar fashion.²⁴¹ The yield of natural isomer **46** formed from the methyl ether of $\Delta^{8(9),14(15)}$ -bisdehydroestradiol analog **45** increases from 22 to 34%, and that of

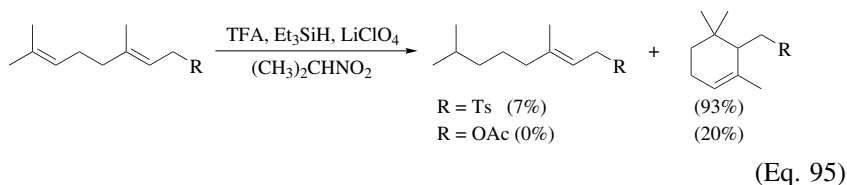
isomer **47** decreases from 78 to 66%, when the solvent is changed from benzene to dichloromethane (Eq. 93).²⁴²



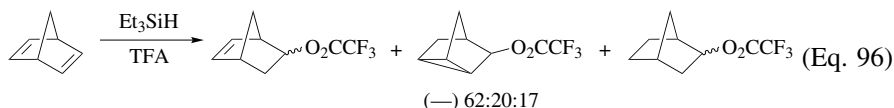
Treatment of linalyl *p*-tolyl sulfone ($\text{R} = \text{SO}_2\text{C}_6\text{H}_4\text{Me-}p$) with 2.5 equivalents of trifluoroacetic acid and two equivalents of triethylsilane in 2-nitropropane containing one equivalent of lithium perchlorate gives, after 20 hours at room temperature, an 87% yield of the product in which only the double bond distal to the sulfone function is reduced (Eq. 94).²⁰⁵



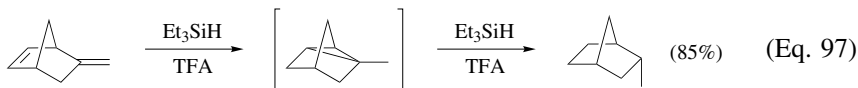
Surprisingly, linalyl acetate ($\text{R} = \text{OAc}$) fails to undergo reduction under these conditions; instead, it rapidly decomposes through cyclization and polymerization pathways.²⁰⁵ The same reaction conditions transform geranyl *p*-tolyl sulfone ($\text{R} = \text{SO}_2\text{C}_6\text{H}_4\text{Me-}p$) into a mixture of 7% reduced and 93% cyclized products within 20 hours, whereas geranyl acetate ($\text{R} = \text{OAc}$) gives only a 20% yield of cyclized and no reduced product (Eq. 95).²⁰⁵



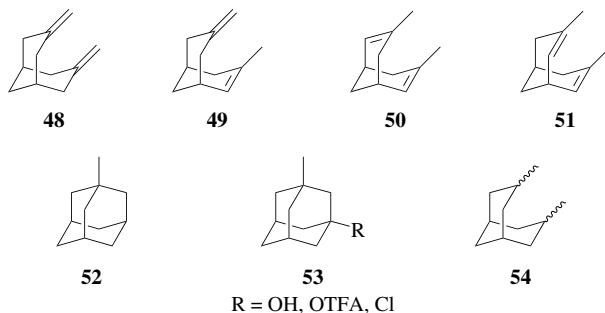
Homoconjugation results in enhanced reactivity of substrates toward ionic hydrogenation. Bicyclo[2.2.1]hepta-2,5-diene forms a mixture of the trifluoroacetate esters of bicyclo[2.2.1]hepten-2-ol, tricyclo[2.2.1.0^{2,6}]heptan-3-ol, and bicyclo[2.2.1]heptan-2-ol in a 62 : 20 : 17 ratio on treatment with 10 equivalents of triethylsilane and 20 equivalents of trifluoroacetic acid for 24 hours at room temperature (Eq. 96).²³⁰



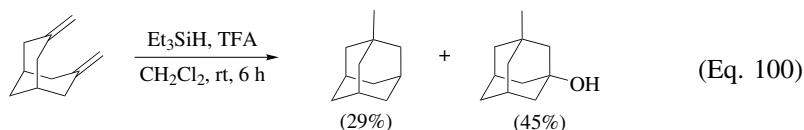
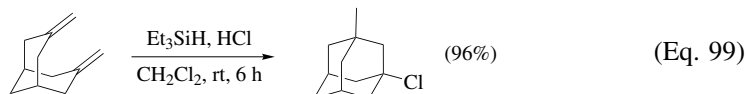
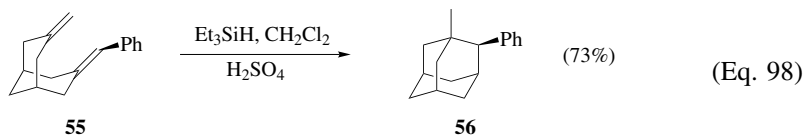
Treatment of 5-methylenebicyclo[2.2.1]hept-2-ene with 10 equivalents of triethylsilane and 20 equivalents of trifluoroacetic acid either for 24 hours at room temperature or 3 hours at 50° gives an 85% yield of completely hydrogenated *endo*-2-methylbicyclo[2.2.1]heptane (Eq. 97). The combination of Et₃SiH/TFA/BF₃•OEt₂ gives this product in 80% yield.²³⁰ The reaction presumably proceeds by way of 2-methyltricyclo[2.2.1.0^{2,6}]heptane as a reaction intermediate, since this compound is expected to rapidly give the same final product when it is subjected to these reaction conditions.²³⁰ The analogous stereospecific behavior is exhibited by 5-ethylidenebicyclo[2.2.1]hept-2-ene.²³⁰



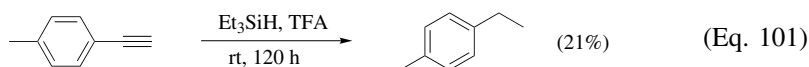
Transannular interactions lead to ring closures and reductions to adamantane compounds when dienes of the bicyclo[3.3.1]nonane family are treated with Brønsted acids and triethylsilane. Compounds **48–51** form reaction mixtures containing various amounts of products **52–54** (R = OH, O₂CCF₃, Cl) under such conditions.²⁴³ The best yields of hydrocarbon **52** occur when the dienes are treated with a 25% excess of sulfuric acid and a 50% excess of triethylsilane in dichloromethane at 20°. ²⁴³ The stereospecific nature of these transannular reductions is demonstrated by the observation that the enantiomeric purity of the chiral diene **55** is retained in the chiral hydrocarbon product **56** (Eq. 98).²⁴³ Dienes of



the type shown can be reduced to the chlorides (Eq. 99).²⁴³ When HCl is replaced with TFA, methyladamantane and methyladamantanol are formed (Eq. 100).

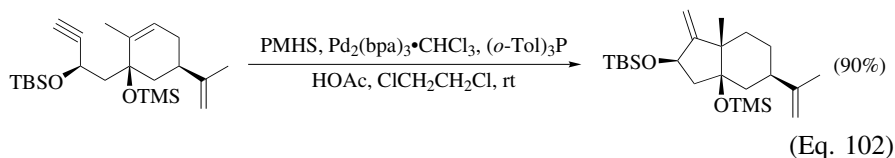


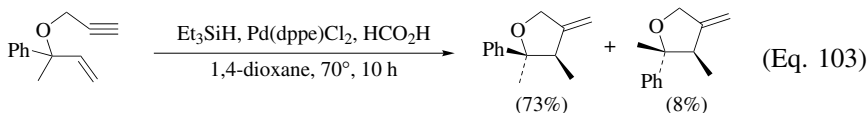
Alkynes to Alkanes. In contrast to the facile ionic hydrogenations that many alkenes undergo, alkynes as a group are very resistant to reduction with the organosilicon hydride/acid combinations. Only those alkynes having an electron-rich aryl group in conjugation with the carbon-carbon triple bond give even modest amounts of reduced products as seen in the example of *p*-tolylacetylene (Eq. 101).²⁴⁴ Alkenes are not observed as products.²⁴⁴



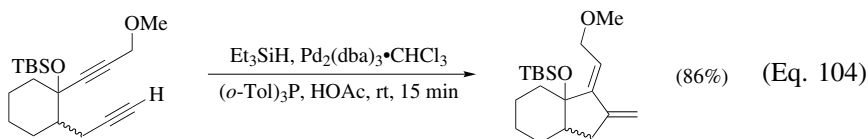
The use of stronger acid conditions provides somewhat better synthetic yields of alkanes from alkynes. A useful method consists of treatment of the substrate with a combination of triethylsilane, aluminum chloride, and excess hydrogen chloride in dichloromethane.¹⁴⁶ Thus, treatment of phenylacetylene with 5 equivalents of triethylsilane and 0.2 equivalents of aluminum chloride in this way at room temperature yields 50% of ethylbenzene after 1.5 hours. Diphenylacetylene gives a 50% yield of bibenzyl when treated with 97 equivalents of triethylsilane and 2.7 equivalents of aluminum chloride after 2.8 hours. Even 1-hexyne gives a mixture of 44% *n*-hexane and 7% methylpentane of undisclosed structure when treated with 10 equivalents of triethylsilane and 0.5 equivalent of aluminum chloride for 0.5 hour.¹⁴⁶

The reductive cyclization of enynes has been used to prepare exo-methylenecycloalkanes. Two systems have proven successful in this transformation, namely PMHS/Pd₂(dba)₃•CHCl₃²⁴⁵ (Eq. 102) and Et₃SiH/Pd(dppe)Cl₂/HCO₂H (Eq. 103).²⁴⁶

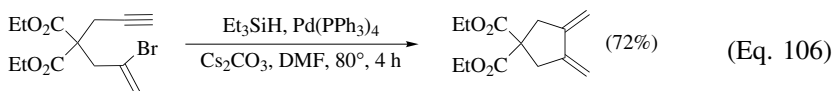
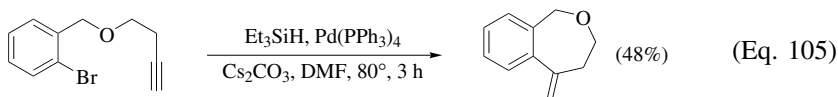




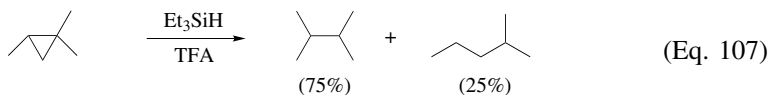
The triethylsilane/ $\text{Pd}_2(\text{dba})_3$ combination is also used for these reductive cyclizations, although lower yields are reported.²⁴⁷ 1,6-Diynes are reductively cyclized to 1,2-dialkylidenecyclopentanes in good yields with $\text{Et}_3\text{SiH}/\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (Eq. 104).²⁴⁸

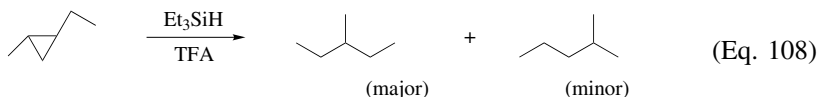


o-Bromobenzyl alkynylalkyl ethers can be reductively cyclized in modest yields with $\text{Et}_3\text{SiH}/\text{Pd}(\text{PPh}_3)_4/\text{Cs}_2\text{CO}_3$ as shown in Eq. 105.²⁴⁹ In a like manner, enynes with a vinyl bromide as the olefin function undergo reductive cyclization (Eq. 106).²⁴⁹

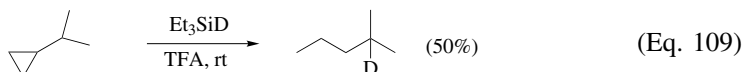


Cyclopropanes to Alkanes. Cyclopropanes that can form ring-opened tertiary aliphatic or benzylic carbenium ion intermediates undergo ionic hydrogenation with reasonable ease when treated with Brønsted acids and organosilicon hydrides. Ring opening occurs preferentially between the most and least highly substituted ring carbons. For example, treatment of 1,1,2-trimethylcyclopropane with one equivalent of triethylsilane and two equivalents of trifluoroacetic acid gives a mixture of 2,3-dimethylbutane (75%) and 2-methylpentane (25%) (Eq. 107).²³³ The conversion into the hydrocarbon mixture is 15% after 15 minutes, 65% after 12 hours, and complete after 16 hours at room temperature.^{222,232} Essentially the same results are obtained when 2,3-dimethyl-2-butene is used as the substrate.²²² The disubstituted isomer 1-methyl-2-ethylcyclopropane gives an alkane reaction mixture consisting primarily of 3-methylpentane along with 2-methylpentane (Eq. 108).²²²

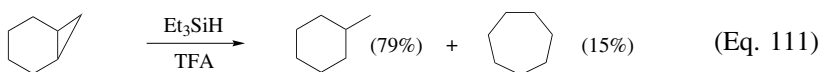
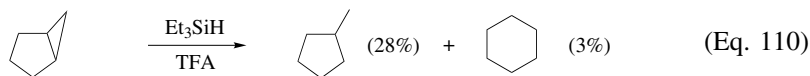




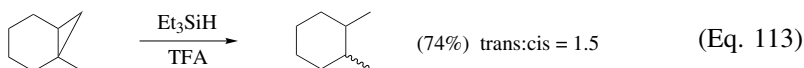
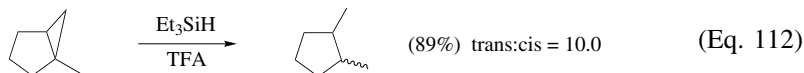
Unlike its disubstituted isomer, the monosubstituted isopropylcyclopropane undergoes reduction to 2-methylpentane to the extent of only 50% after 24 hours (Eq. 109),²³² a result similar to that observed when 2-methyl-1-pentene is the substrate.²²² It is interesting that deuterated triethylsilane produces 2-methylpentane that contains the deuterium label only at the C2 position.²⁵⁰ This label position suggests that in this reaction ring protonation and opening are followed by a 1,2-hydride shift that precedes capture by the silyl hydride of any initially formed carbocation intermediates.²⁵⁰ Ethylcyclopropane, with an unbranched side chain, shows no sign of reduction under these conditions even after 200 hours.²³² Phenylcyclopropane is reduced to 1-phenylpropane.²²²



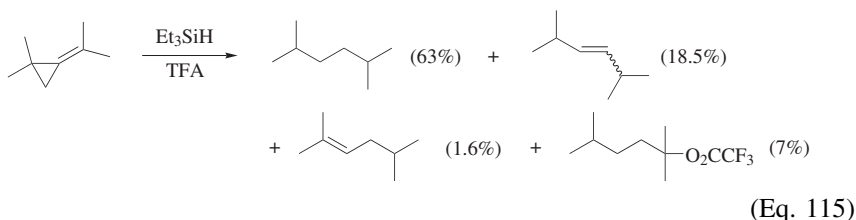
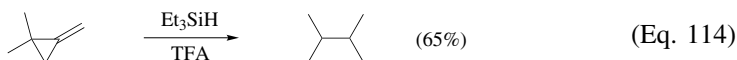
Bicyclic hydrocarbons that contain a three-membered ring slowly undergo ionic hydrogenation when treated with at least one equivalent of triethylsilane and an excess of trifluoroacetic acid at room temperature.²²⁹ Thus, bicyclo[3.1.0]hexane gives a product mixture containing methylcyclopentane (28%) and cyclohexane (3%) when reacted with one equivalent of triethylsilane and four equivalents of trifluoroacetic acid for 140 hours (Eq. 110). The main products are the trifluoroacetates of cyclohexanol and *cis*- and *trans*-2-methylcyclopentanol in a ratio of 10:35.²²⁹ Under the same conditions, bicyclo[4.1.0]heptane yields a mixture containing mainly methylcyclohexane (79%) with some cycloheptane (5%) and the corresponding trifluoroacetates (16%) (Eq. 111).²²⁹



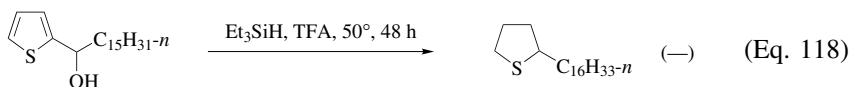
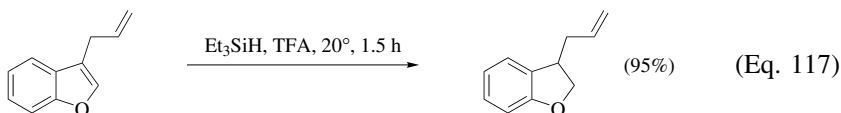
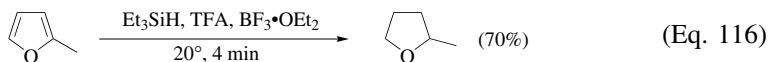
After ten days at room temperature in the presence of one equivalent of triethylsilane and two equivalents of trifluoroacetic acid, both 1-methylbicyclo[3.1.0]hexane and 1-methylbicyclo[4.1.0]heptane form mixtures of the two isomers of their respective 1,2-dimethylcycloalkanes (Eqs. 112 and 113).²²⁹



Based on the few reported examples, the pattern of ring cleavage that accompanies the ionic hydrogenation of alkylidenecyclopropanes seems to be related to the pattern and degree of substitution on both the ring and the double bond.²³³ Thus, treatment of 1,1-dimethyl-2-methylenecyclopropane with two equivalents of triethylsilane and four equivalents of trifluoroacetic acid for 90 hours at room temperature yields 65% of 2,3-dimethylbutane (Eq. 114).²²⁹ Exposure of 1,1-dimethyl-2-isopropylidenecyclopropane to the same ratio of reactants at 50° for 16 hours produces a complex mixture containing 63% of 2,5-dimethylhexane, 18.5% of 2,5-dimethyl-3-hexene, 1.6% of 2,5-dimethyl-2-hexene, and 7% of 2,5-dimethyl-2-hexyl trifluoroacetate (Eq. 115).²²⁹

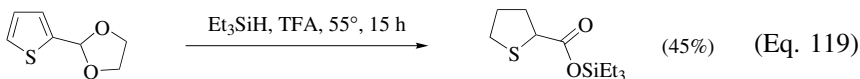


Aromatic Substrates. Aromatic hydrocarbons can be reduced with organosilanes to dienes, alkenes, or alkanes. The combination of Et₃SiH/TFA/BF₃•OEt₂ reduces furans to tetrahydrofurans in good yields (Eq. 116).²¹¹ In general, poor yields are obtained with the Et₃SiH/TFA reduction of benzofurans,²⁵¹ but the C3-substituted benzofuran shown undergoes reduction of the furan ring in excellent yield with this reagent (Eq. 117).²⁵² Similarly, benzothiophenes are reduced in 60 to 90% yields under the same conditions.²⁵³ The Et₃SiH/TFA system reduces thiophenes to tetrahydrothiophenes in good yields.^{254–257} In α-hydroxy thiophenes, both double bonds of the thiophene unit and the hydroxy group are reduced (Eq. 118).²⁵⁸

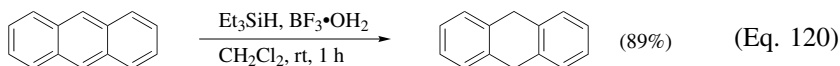


Similar reactivity is realized with 2-acetylthiophene using triethylsilane with aluminum chloride.²⁵⁹ Treatment of the ethylene glycol acetal of 2-thiophenecarbaldehyde with Et₃SiH/TFA results in reduction of the ring and oxidation of the side chain to the silylated carboxylic acid (Eq. 119),²⁶⁰ whereas similar treatment of 2-thiophenecarbaldehyde gives 2-methyltetrahydrothiophene and 2-

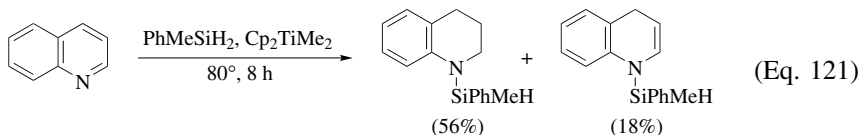
acetylthiophene gives 2-ethylthiophene.²⁵⁷ Some thiophenes are reduced to a mixture of tetrahydrothiophenes and 2,5-dihydrothiophenes.^{210,259,261}



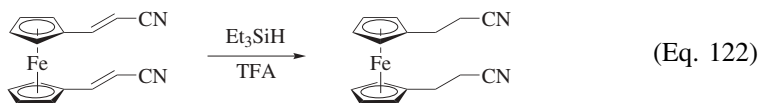
Partial reduction of polyarenes has been reported. Use of boron trifluoride hydrate ($\text{BF}_3 \cdot \text{OH}_2$) as the acid in conjunction with triethylsilane causes the reduction of certain activated aromatic systems.^{217,262} Thus, treatment of anthracene with a 4–6 molar excess of $\text{BF}_3 \cdot \text{OH}_2$ and a 30% molar excess of triethylsilane gives 9,10-dihydroanthracene in 89% yield after 1 hour at room temperature (Eq. 120). Naphthacene gives the analogously reduced product in 88% yield under the same conditions. These conditions also result in the formation of tetralin from 1-hydroxynaphthalene (52%, 4 hours), 2-hydroxynaphthalene (37%, 7 hours), 1-methoxynaphthalene (37%, 10 hours), 2-methoxynaphthalene (26%, 10 hours), and 1-naphthalenethiol (13%, 6 hours). Naphthalene, phenanthrene, 1-methylnaphthalene, 2-naphthalenethiol, phenol, anisole, toluene, and benzene all resist reduction under these conditions.²¹⁷ Use of deuterated triethylsilane to reduce 1-methoxynaphthalene gives tetralin-1,1,3,3- d_4 as product, thus yielding information on the mechanism of these reductions.²⁶² 2-Mercaptonaphthalenes are reduced to 2,3,4,5-tetrahydronaphthalenes in poor to modest yields.^{217,263}



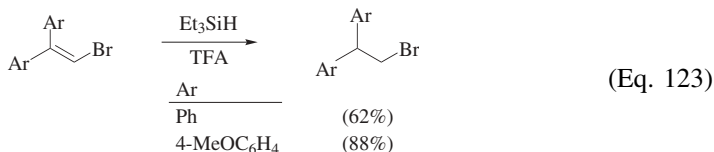
The combination of PhMeSiH_2 (or Ph_2SiH_2) and Cp_2TiMe_2 (10 mol%) reduces pyridines to N-silylated-di- or tetrahydropyridines or the N-silylated piperidines.^{264,265} With quinoline, only the pyridine ring is reduced preferentially to the benzene ring (Eq. 121).



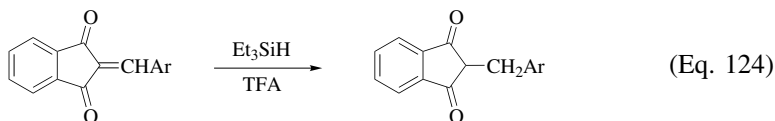
Miscellaneous Unsaturated Substrates. Exposure of 1,1'-bis(*trans*-2-cyanovinyl)ferrocene to a mixture of two equivalents of triethylsilane and 320 equivalents of trifluoroacetic acid at 50° for three hours gives a product with the carbon-carbon double bonds reduced in 83% yield, but leaving the nitrile groups intact (Eq. 122).¹⁷⁹



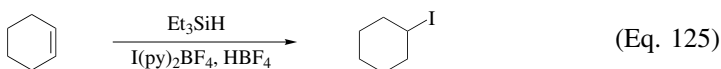
Treatment of a chloroform or dichloromethane solution of 1-bromo-2,2-diphenylethene or 1-bromo-2,2-bis(4'-methoxyphenyl)ethene with a slight excess of triethylsilane and a 9- to 10-fold excess of TFA gives the corresponding ethanes in 62% and 88% yields, respectively, after one hour at 0° (Eq. 123).¹⁸⁴



The carbonyl groups of 1,3-indanediones are generally resistant to the action of combinations of acid and silanes at room temperature.²⁶⁶ Accordingly, treatment of a variety of 2-benzylidene-1,3-indanediones with Et₃SiH/TFA (ratio of 1:5:10) in CCl₄ at 55° for 7–20 hours gives the corresponding substituted 2-benzyl-1,3-indanediones in 54–78% yields (Eq. 124).²⁶⁶ Use of a 27-fold excess of trifluoroacetic acid in the absence of a cosolvent reportedly leads to reduction of the carbonyl groups to give a mixture of products.²⁶⁷

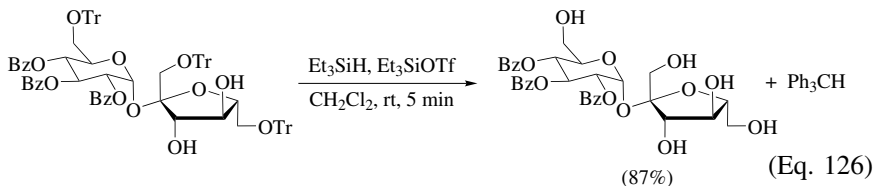


An interesting hydroiodination reaction occurs when a mixture of cyclohexene and triethylsilane in dichloromethane is treated with a mixture of bis(pyridine) iodonium tetrafluoroborate and tetrafluoroboric acid in diethyl ether (Eq. 125). A 50% yield of iodocyclohexane is produced after one hour at 20°.²⁶⁸

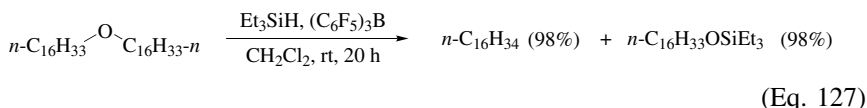


Reduction of Ethers

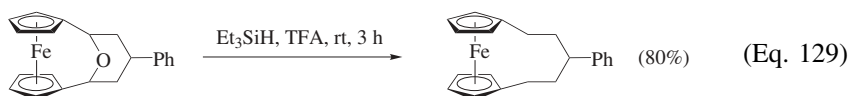
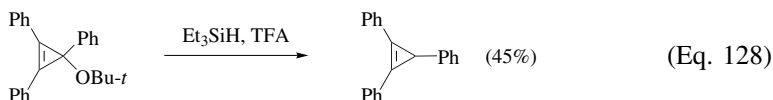
Because of the high stability of the triphenylmethyl carbocation, the reductive ether cleavage of trityl ethers with Et₃SiH/trimethylsilyl triflate (TMSOTf) is highly successful. This reaction even occurs in the presence of highly reactive sugar ketals, leaving the ketals intact (Eq. 126).²⁶⁹



The combination of PMHS and Pd(PPh₃)₄ reduces allyl ethers to propene and alcohols.²⁷⁰ The best combination for the reductive cleavage of ethers appears to be Et₃SiH/(C₆F₅)₃B, which gives excellent yields of the alcohol (via the silyl ether) and alkane (Eq. 127).¹⁴⁵

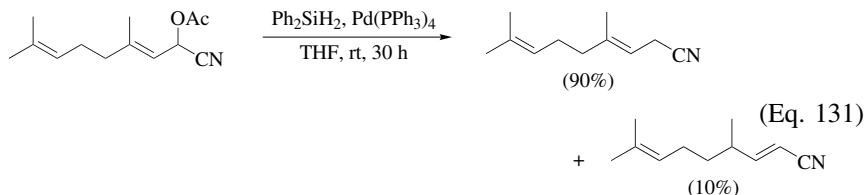
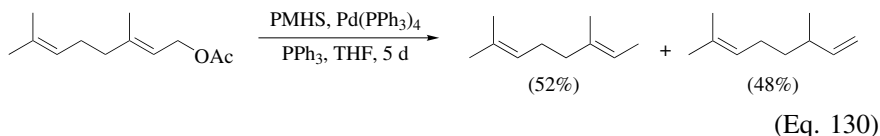


Dialkyl ethers are reduced with the combination of $\text{Et}_3\text{SiH/TFA}$, although the yields vary.^{144,271} *tert*-Butyl triphenylcyclopropenyl ether is reduced to the corresponding cyclopropene (Eq. 128),²⁷² and a dibenzyl-like ferrocene-derived ether is reduced to the corresponding alkane (Eq. 129).¹⁷⁹

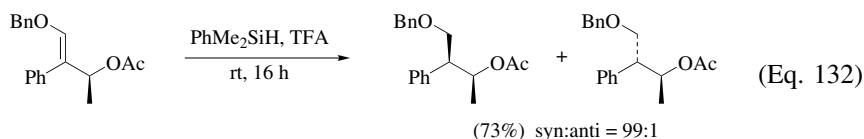


Reduction of Allyl Acetates

Allyl acetates are reduced to the corresponding olefins with $\text{PMHS/Pd(PPh}_3)_4$ or $\text{Ph}_2\text{SiH}_2/\text{Pd(PPh}_3)_4$.^{196,273} Unfortunately, double bond migration occurs in many of these reactions (Eqs. 130 and 131).^{196,273} The combinations of $\text{Ph}_2\text{SiH}_2/\text{Pd(P(Tol-}i{p})_3)_4/\text{ZnCl}_2$ ²⁷⁴ and $\text{Et}_3\text{SiH/TFA}$ ²⁷⁵ are also employed in this transformation.



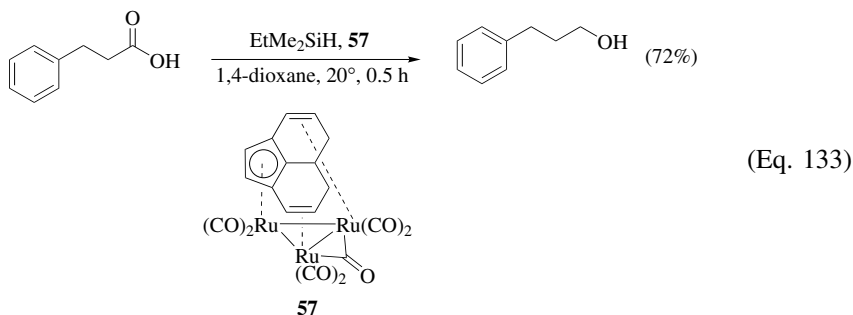
The $\text{Et}_3\text{SiH/TFA}$ reduction of a 3-acetoxy enol ether is reported. The diastereoselectivity is high for the *Z* isomer, but much lower for the *E* isomer (Eq. 132).²⁷⁶



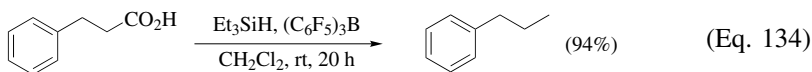
Reduction of Carboxylic Acids

Aromatic and aliphatic carboxylic acids are reduced to the trifluoroacetates of the alcohol with $\text{Et}_3\text{SiH/TFA}$.²⁷⁷ Use of an excess of the triethylsilane can give

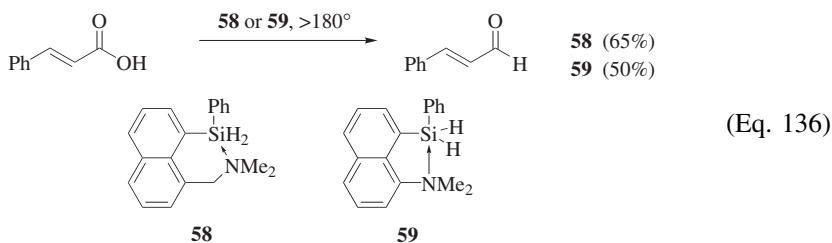
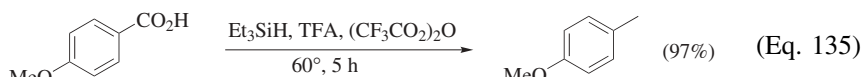
further reduction to the methyl group. The combination of PMHS/TBAF (tetra-*n*-butylammonium fluoride) reduces benzoic acids to the benzyl alcohols in good yields.²⁷⁸ Comparable yields of this useful transformation can be realized through the use of PMHS/Ti(OPr-*i*)₄ (or PMHS/Ti(OEt)₄).²⁷⁹ Both aromatic and aliphatic carboxylic acids can be reduced with EtMe₂SiH and the ruthenium-based catalyst **57** (Eq. 133).²⁸⁰ The latter reagent/catalyst combination also reduces esters to alcohols in high yield.



The highly reactive reagent combination of Et₃SiH/(C₆F₅)₃B reduces carboxylic acids to methyl groups (Eq. 134).^{281,282} Isolation of the intermediate silyl ether is also possible.²⁸²

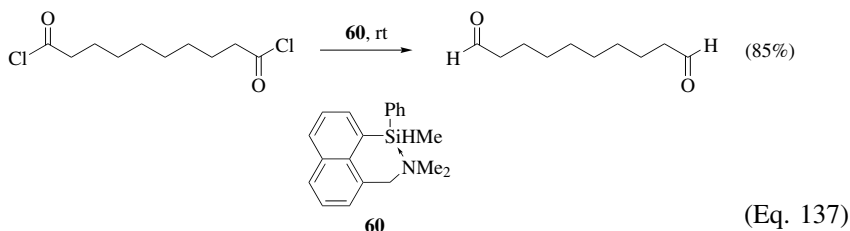


Benzoic acids with electron-donating groups on the ring are reduced to toluene derivatives with the reagent combination Et₃SiH/TFA/TFAA.²⁸³ *p*-Anisic acid gives 4-methylanisole in 97% yield under these conditions (Eq. 135). Formation of the corresponding benzyl trifluoroacetates occurs for substrates without activating groups. *p*-Nitrobenzoic acid is unreactive under these conditions, as are dibasic acids such as phthalic or succinic acid.²⁸³ The same conditions reduce alkyl carboxylic acids to trifluoroacetates.²⁷⁷ Use of the silane **58** or **59** provides cinnamaldehyde in fair yield from cinnamic acid (Eq. 136).²⁸⁴

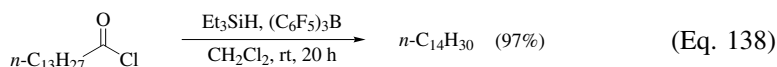


Reduction of Acid Halides and Acid Anhydrides

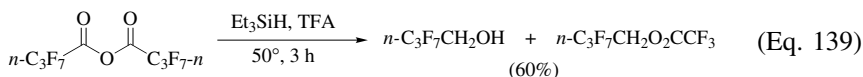
The organosilane reduction of acid chlorides to aldehydes has been accomplished in high yields with the use of the pentacoordinated organosilane **60** (Eq. 137).¹⁰⁷ This transformation has been reported to occur with tribenzylsilane and triethylsilane, but yields were not reported.^{285,286}



The combination $\text{Et}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$ reduces acid chlorides to methyl groups (Eq. 138).^{281,282} If a smaller amount of triethylsilane is used, the same combination reduces aryl acid chlorides to the trimethylsilyl ethers of the benzyl alcohols.^{281,282}

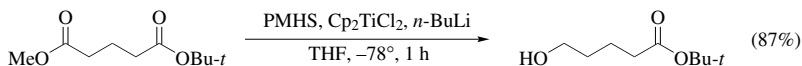
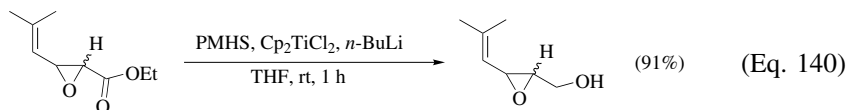


One study of the $\text{Et}_3\text{SiH}/\text{TFA}$ reduction of acid anhydrides reports the formation of one equivalent each of the alcohol and the trifluoroacetate ester of the acid (Eq. 139).²⁸⁷



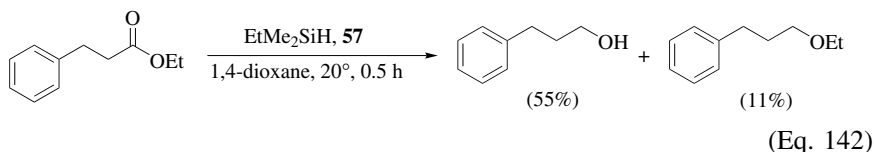
Reduction of Esters and Lactones

The combination of $(\text{EtO})_3\text{SiH}/\text{CsF}$ (or KF) provides a convenient reagent for the reduction of esters to alcohols.^{76,80,83} The yields are in the 70% range. Potassium tetraethoxyhydridosilicate also reduces esters in moderate yields.²⁸⁸ The combination of $\text{PMHS}/\text{Cp}_2\text{TiCl}_2/n\text{-BuLi}$ reduces esters in high yields even in the presence of an epoxide and a trisubstituted olefin (Eq. 140).²⁸⁹ The reagent combination can reduce a methyl ester in the presence of a *tert*-butyl ester (Eq. 141).²⁹⁰

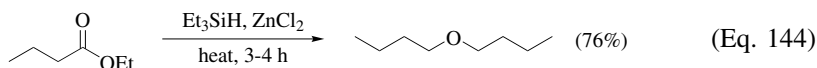
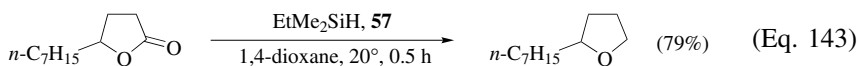


(Eq. 141)

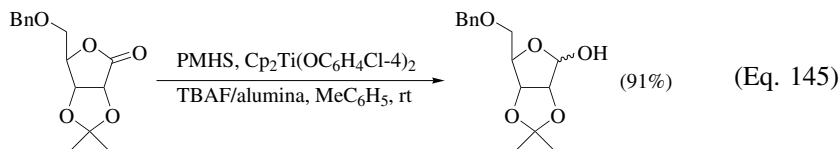
Ester reductions with $(\text{EtO})_3\text{SiH}/(\text{EBTHI})\text{TiCl}_2/n\text{-BuLi}$ (EBTHI = ethylene-bis(η^5 -tetrahydroindenyl)titanium) result in good yields of the corresponding alcohols.²⁹⁰ Excellent yields of alcohols result from the reduction of esters with the PMHS/ $\text{Ti}(\text{OPr-}i)_4$ system.^{279,291,292} The reaction catalyzed by $(\text{EBTHI})\text{TiCl}_2/n\text{-BuLi}$ occurs in lower yields.²⁸⁹ Methyl cinnamate is reduced with PMHS/TBAF in good yield.²⁷⁸ The ruthenium complex **57** (Eq. 135) catalyzes the EtMe_2SiH reduction of esters to alcohols, although a mixture of the alcohol and the ether are often obtained (Eq. 142).²⁸⁰



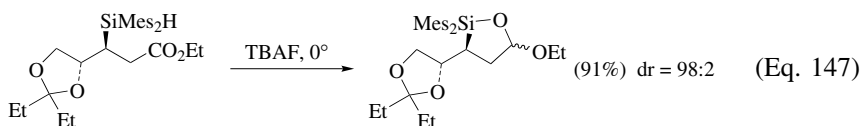
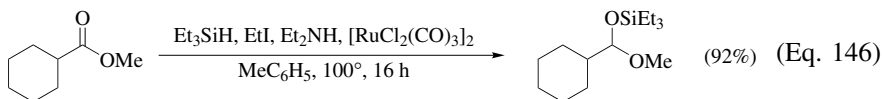
High yields in the reduction of esters with $\text{Ph}_2\text{SiH}_2/[\text{RhCl}(\text{cod})]_2$ are reported.²⁹³ The combination of $(\text{MeO})_3\text{SiH}/\text{LiOMe}$ is reported to reduce esters to the alcohols, although the advantages of this system over others does not seem to warrant working with the highly hazardous trimethoxysilane.²⁹⁴ The reduction of the carbonyl group of an ester or lactone is possible. This results in the formation of the corresponding ether. This reaction can be carried out employing $\text{PhSiH}_3/(\text{PPh}_3)(\text{CO})_4\text{MnC}(\text{O})\text{Me}$,²⁹⁵ $\text{PhSiH}_3/\text{Mn}(\text{CO})_5\text{Br}$,²⁹⁵ $\text{Cl}_3\text{SiH}/\gamma$ -irradiation,²⁹⁶ or $\text{Et}_3\text{SiH}/\text{TiCl}_4/\text{TMSOTf}$.²⁹⁷ The reduction of lactones to cyclic ethers is nicely accomplished with the EtMe_2SiH /ruthenium catalyst system **57** (Eq. 143).²⁸⁰ The same transformation can be carried out with $\text{Et}_3\text{SiH}/\text{TiCl}_4$ ²⁹⁷ or $\text{PhSiH}_3/\text{Mn}(\text{CO})_5\text{Br}$.²⁹⁵ The reductive etherification of esters occurs by treating an ester with $\text{Et}_3\text{SiH}/\text{ZnCl}_2$ (Eq. 144).²⁹⁸



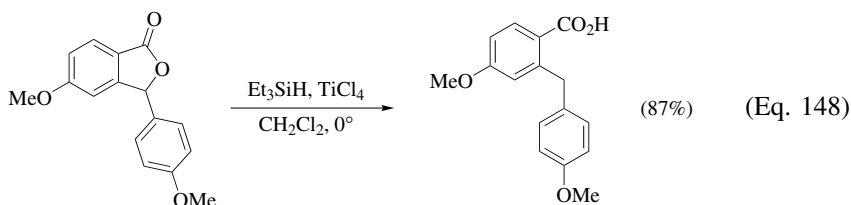
The reduction of esters to aldehydes is a useful transformation and can be accomplished in good yields with $\text{Et}_3\text{SiH}/[\text{RuCl}_2(\text{CO})_3]_2$ ²⁹⁹ or with $\text{Ph}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$.¹¹⁶ Thio esters are reduced to aldehydes in good yields with $\text{Et}_3\text{SiH}/\text{Pd/C}$.³⁰⁰ Lactones can be reduced to hemiacetals with PMHS/ Cp_2TiF_2 or PMHS/ $\text{Cp}_2\text{Ti}(\text{OC}_6\text{H}_4\text{Cl-4})_2$ (Eq. 145).^{301,302}



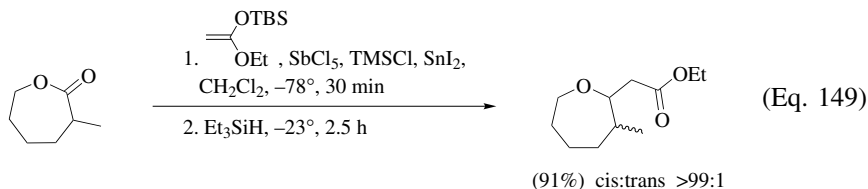
The reduction of an ester to the silylated acetal occurs with $\text{Et}_3\text{SiH}/\text{Et}_2\text{NH}/[\text{RuCl}_2(\text{CO})_3]_2$ (and other Ru catalysts) (Eq. 146),²⁹⁹ $\text{Et}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$,^{281,282} or $\text{Ph}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$,¹¹⁵ and with $\text{Ph}_2\text{MeSiH}/\text{Mn}(\text{CO})_5\text{C}(\text{O})\text{Me}$.²⁹⁵ The latter system reduces methyl benzoate to toluene. An intramolecular version of the ester to silylated acetal transformation is effected with TBAF (Eq. 147).^{303,304}



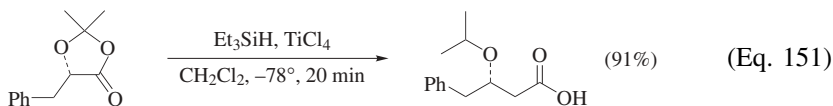
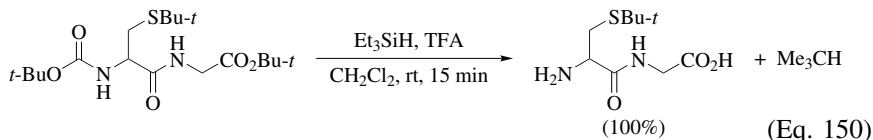
The reaction of lactones of benzyl alcohols with $\text{Et}_3\text{SiH}/\text{TFA}$ results in complete reduction of the alcohol part of the lactone to the methylene group while preserving the carboxylate function (Eq. 148).³⁰⁵



The β -hydroxy ester resulting from the reaction of the *tert*-butyldimethylsilyl ketene acetal of ethyl acetate with a lactone under acid conditions can be reduced to the β -alkoxy ester.³⁰⁶ The overall yields are excellent (Eq. 149).



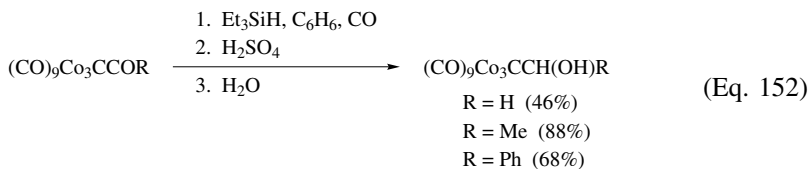
The reaction of *tert*-butyl esters with $\text{Et}_3\text{SiH}/\text{TFA}$ results in the reductive deprotection of the ester and formation of isobutane. The yields of the isobutane are not recorded, but the acids are obtained nearly quantitatively (Eq. 150).³⁰⁷ In a similar manner, the lactone shown in Eq. 151 is converted into the acid in good yield.³⁰⁸ In like manner, the reductive deprotection of allyl esters provides the carboxylic acids in high yields.²⁷⁰



The reduction of trifluoroacetates to alkanes occurs with the trifluoroacetates of benzylic and tertiary alcohols. This transformation is reported to occur with reagent combinations such as Ph_3SiH /nitrobenzene¹⁹³ and $\text{EtCl}_2\text{SiH}/\text{AlBr}_3$.¹⁹² Secondary trifluoroacetates give more modest yields.¹⁹²

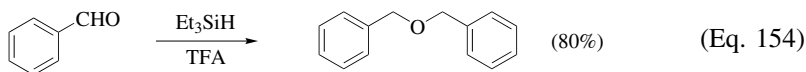
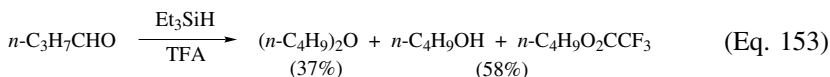
Reduction of Aldehydes

Reduction to Alcohols. Aldehydes do not normally react spontaneously with organosilicon hydrides to form alcohols. Exceptional behavior is displayed with organocobalt cluster complex carbonyl compounds, which form the corresponding alcohols ($\text{R} = \text{H}, \text{Me}, \text{Ph}, \text{etc.}$) after treatment with one equivalent of triethylsilane in refluxing benzene under a carbon monoxide atmosphere and acid workup (Eq. 152).^{309,310} Aside from these specific examples of anomalous behavior, the generally observed lack of reactivity is due to the combination of the relatively weak electrophilicity of the aldehyde carbonyl carbon center and the extremely feeble nucleophilicity of most tetravalent silyl hydrides. The reduction of aldehyde carbonyl groups by organosilicon hydrides can be promoted by several means. One way is by the introduction of acidic or electrophilic substances that coordinate with the carbonyl oxygen and thereby enhance the electrophilicity of the carbonyl carbon toward receiving a weakly nucleophilic silyl hydride. As mentioned previously, a second way is through the introduction into the reaction medium of substances possessing high nucleophilicity toward silicon centers. Such substances are thought to activate the silyl hydride by forming valence-expanded silicon species with enhanced hydride-donating properties capable of attacking even weakly electrophilic centers such as the carbonyl groups of common aldehydes. Both means of promotion can be synthetically useful.

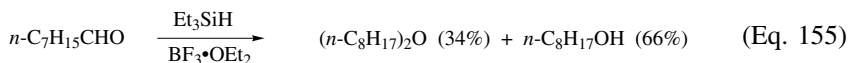


Promotion by Acid. In principle, the reduction of aldehydes to alcohols and alcohol derivatives by organosilicon hydrides should occur upon exposure to either Lewis or Brønsted acids, as represented in Eq. 2. In practice, although

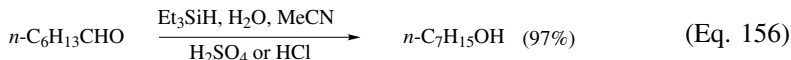
organosilicon hydride reductions of either aliphatic or aromatic aldehydes do occur rapidly under acid conditions, they are frequently complicated by the formation of other products. The reductions rarely give clean yields of alcohols when conducted under anhydrous conditions. The reaction of a mixture of 1-butanal and triethylsilane that occurs upon addition of excess trifluoroacetic acid is a typical example. Analysis of the reaction mixture immediately following the addition of acid shows the formation of 37% of di-*n*-butyl ether along with *n*-butyl alcohol and *n*-butyl trifluoroacetate in a combined yield of 58% (Eq. 153).³¹¹ No unreacted aldehyde remains. The same process transforms benzaldehyde into dibenzyl ether in 80% yield (Eq. 154).^{311,312} In both reactions, the silicon-containing products are triethylsilyl trifluoroacetate and hexaethyldisiloxane. The Et₃SiH/TFA combination can also lead to the trifluoroacetate and toluene derivatives when used with some aryl aldehydes.⁶⁹



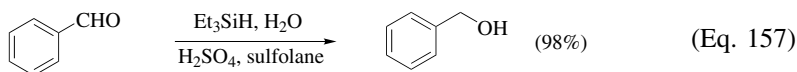
The reduction of aldehydes with the combination Et₃SiH/BF₃•OEt₂ gives both the alcohol and the symmetrical ether,⁷⁰ as do the Et₃SiH/TFA (and other acids) combinations.³¹³ Addition of boron trifluoride etherate to a mixture of 1-octanal and triethylsilane leads to the formation of di-*n*-octyl ether in 66% yield and *n*-octyl alcohol in 34% yield (Eq. 155).⁷⁴



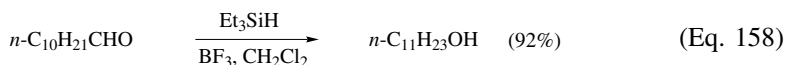
The addition of water and a non-hydrogen-bonding solvent to the reduction medium causes the reactions to shift toward the formation of alcohol products.³¹³ For example, triethylsilane in a mixture of concentrated hydrochloric acid and acetonitrile (5 : 4) reduces 1-heptanal to 1-heptanol in quantitative yield after 3 hours at room temperature. In a mixture of triethylsilane in sulfuric acid, water, and acetonitrile (2 : 2 : 5), *n*-heptanal gives a 97% yield of the same alcohol after 1.25 hours (Eq. 156).³¹³



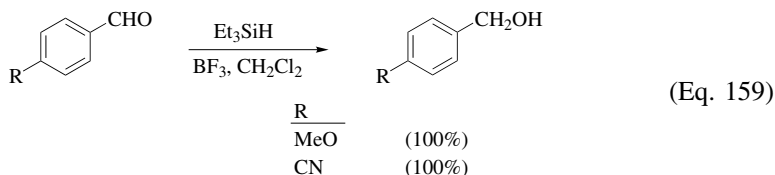
Triethylsilane reduces benzaldehyde to benzyl alcohol in 98% yield after 32 hours in a reaction medium containing sulfuric acid, water, and sulfolane (1 : 2 : 5) (Eq. 157). Neither benzene nor dimethylformamide is effective as an interfacing solvent for producing alcohol products under these conditions.³¹³



In contrast to the propensity of Brønsted and some Lewis acids such as boron trifluoride etherate to promote the organosilicon hydride reduction of aldehydes to ethers under anhydrous conditions, uncomplexed boron trifluoride used with triethylsilane in dichloromethane solvent leads to the formation of primary alcohols in good yields from aliphatic aldehydes and from aromatic aldehydes containing electron-withdrawing groups.¹ The success of this method depends on the absence of significant quantities of Brønsted acids in the reaction medium and requires that the boron trifluoride gas be scrubbed of hydrogen fluoride prior to introduction. Using this method, 1-undecanal gives a 92% isolated yield of 1-undecanol after only 10 minutes at 0° (Eq. 158).



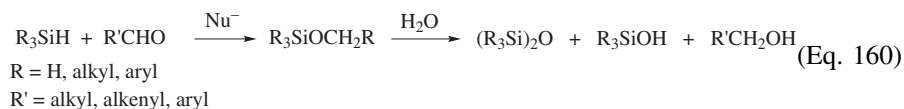
The same technique causes the transformation of *p*-anisaldehyde (R = MeO) and *p*-cyanobenzaldehyde (R = CN) into the corresponding substituted benzyl alcohols in quantitative yields within 10 minutes at 0° (Eq. 159).¹ The reduction of aryl aldehydes to benzyl alcohols without over-reduction to the arylmethanes also occurs with the reagent combinations PMHS/TBAF,²⁷⁸ PMHS/Triton® B,²⁷⁸ and Ph₃SiH/(C₆F₅)₃B.¹¹⁶ The Ph₃SiH/(C₆F₅)₃B combination can be used to isolate the benzyl silyl ethers.²⁸² Treatment of *p*-nitrobenzaldehyde (R = NO₂) with a catalytic amount of the Lewis acid trimethylsilyl iodide (TMSI, generated in situ from trimethylsilyl chloride and sodium iodide) and tetramethyldisiloxane gives the benzyl alcohol in 91% isolated yield.³¹⁴



The reagent combinations PMHS/ZnCl₂,³¹⁵ PMHS/[Bu₂(AcO)Sn]₂O,³¹⁶ and PMHS/HCuPPh₃³¹⁷ all promote reduction of aldehydes to the corresponding alcohols in good yields. Trichlorosilane in dimethylformamide reduces aldehydes to alcohols in high yields.³¹⁸

Promotion by Valence Expansion. Addition of nucleophilic substances to mixtures of aldehydes and organosilicon hydrides promotes the reduction of the carbonyl group as depicted previously in Eq. 6. The reductions can occur under homogeneous⁸³ or heterogeneous^{79,80,319} conditions, both with^{83,320} and without solvent.^{83,319} When the reactions occur under anhydrous conditions with catalytic amounts of nucleophile, the first-formed product is frequently a silyl ether. This ether can be regarded as an intermediate that normally undergoes facile acid- or base-catalyzed hydrolysis to give a final alcohol product (Eq. 160).⁸⁰ The silicon-containing products are usually silanols and/or disiloxanes produced by

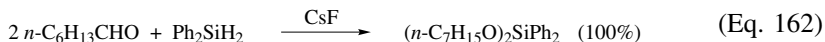
hydrolysis of the intermediate silyl ethers. These reductions are normally quite chemoselective and tolerate many other functional groups.



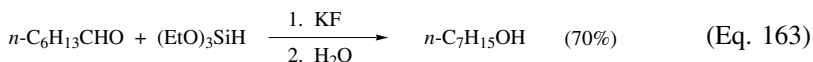
Fluoride ion is effective in promoting the reduction of aldehydes by organosilicon hydrides (Eq. 161). The source of fluoride ion is important to the efficiency of reduction. Triethylsilane reduces benzaldehyde to triethylbenzyloxysilane in 36% yield within 10–12 hours in anhydrous acetonitrile solvent at room temperature when tetraethylammonium fluoride (TEAF) is used as the fluoride ion source and in 96% yield when cesium fluoride is used.⁸³ The carbonyl functions of both *p*-anisaldehyde and cinnamaldehyde are reduced under similar conditions. Potassium bromide or chloride, or tetramethylammonium bromide or chloride are not effective at promoting similar behavior under these reaction conditions.⁸³ Moderate yields of alcohols are obtained by the KF-catalyzed PMHS, (EtO)₃SiH, or Me(EtO)₂SiH reduction of aldehydes.^{80,83,79}



Diphenylsilane reacts with two equivalents of neat *n*-heptanal in the presence of anhydrous cesium fluoride within three minutes at room temperature to form di-*n*-heptoxydiphenylsilane quantitatively (Eq. 162).³¹⁹ Potassium fluoride and potassium phthalate are considerably less effective promoters, even at temperatures up to 140°.³¹⁹



Alkoxy-substituted organosilicon hydrides are more reactive toward carbonyl functions in the presence of nucleophiles than are organosilicon hydrides that have only alkyl or aryl substituents at the silicon center. The order of reactivity of the silanes used is (EtO)₃SiH > (EtO)₂SiMeH, and that of the fluoride salts is CsF > KF.⁸³ The use of these silane/fluoride salt pairs can lead to some very chemoselective transformations.^{79,80,319} For example, after hydrolytic workup, an equimolar mixture of benzaldehyde, diethoxymethylsilane, and cesium fluoride gives an 80% yield of benzyl alcohol after only 10 minutes at room temperature under heterogeneous conditions.⁸⁰ The use of triethoxysilane and potassium fluoride gives a 90% yield of benzyl alcohol after six hours at room temperature. The same combination of reagents converts 1-heptanal into 1-heptanol in 70% yield within four hours without affecting benzophenone or 1,3-diphenylpropan-2-one when either is added to the same reaction mixture (Eq. 163).⁸³

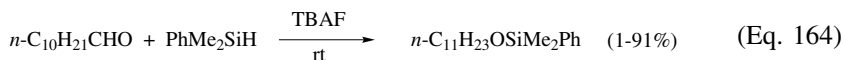


These reaction conditions also permit the chemoselective quantitative reduction of benzaldehyde to benzyl alcohol without any concomitant reduction of either acetophenone or 3,3-dimethylbutan-2-one present in the same reaction mixture.⁸³ Additionally, this useful method permits the reduction of aldehyde functions in polyfunctional compounds without affecting amide, anhydride, ethylenic, bromo, chloro, or nitro groups.^{79,80,319}

An improved variation of this reduction method involves the use of potassium fluoride (either anhydrous or as the dihydrate) or potassium formate in a polar aprotic solvent such as dimethylformamide or dimethyl sulfoxide in conjunction with either diethoxymethylsilane or PMHS. The intermediate silyl ethers are worked up by acidic hydrolysis when diethoxymethylsilane is used and by methanolysis when PMHS is the reducing agent.⁸² A high chemoselectivity among carbonyl group reductions may be accomplished using this method by adjusting the reaction conditions. Aldehydes are especially easy to reduce this way.

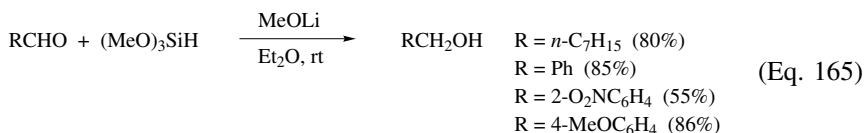
The combination of diethoxymethylsilane and KF in dimethylformamide produces a 90% yield of benzyl alcohol from benzaldehyde in 0.25 hour at 20° following workup.⁸² In a similar way, 1-heptanal forms 1-heptanol in 85% yield within 1.75 hours at 10°. Other combinations of the salts, solvents, and organosilicon hydrides give useful, if somewhat lower, yields of products. Potassium fluoride dihydrate, although a more active catalyst than the anhydrous salt, requires use of an excess of organosilicon hydride because the water that is present destroys some of the silane. Use of potassium formate and PMHS in dimethylformamide permits facile selective reduction of both alkyl and aryl aldehydes in the presence of ketones and esters.⁸² The system of Me(EtO)₂SiH and KO₂CH is very selective toward the reduction of aldehydes in the presence of ketones.⁸² In a similar approach aldehydes are reduced with [HSi(OEt)₄]K.²⁸⁸

Fluoride ion catalyzes the hydrosilylation of both alkyl and aryl aldehydes to silyl ethers that can be easily hydrolyzed to the free alcohols by treatment with 1 M hydrogen chloride in methanol.³²⁰ The most effective sources of fluoride are TBAF and tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF). Somewhat less effective are CsF and KF. Solvent effects are marked. The reactions are facilitated in polar, aprotic solvents such as hexamethylphosphortriamide (HMPA) or 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), go moderately well in dimethylformamide, but do not proceed well in either tetrahydrofuran or dichloromethane. The solvent effects are dramatically illustrated in the reaction of undecanal and dimethylphenylsilane to produce undecyloxyphenyldimethylsilane. After one hour at room temperature with TBAF as the source of fluoride and a 10 mol% excess of silane, yields of 91% in HMPA, 89% in DMPU, 56% in dimethylformamide, 9% in tetrahydrofuran, and only 1% in dichloromethane are obtained (Eq. 164).³²⁰

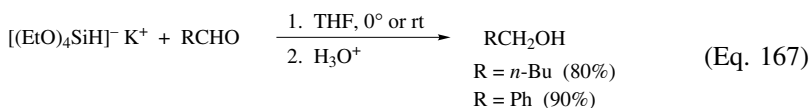
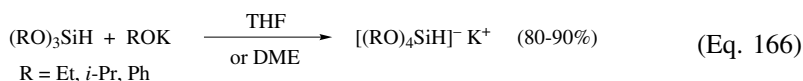


The reduction of aldehydes to alcohols takes place under mild conditions upon treatment with a mixture of trimethoxysilane and lithium methoxide (20 mol%

excess of each) in diethyl ether at room temperature (Eq. 165). The reaction occurs with both alkyl and aryl aldehydes and can be used to reduce aldehydes in the presence of ketones, esters, and nitriles. Workup is by treatment with 1 M aqueous hydrochloric acid.⁹¹ For example, benzaldehyde forms benzyl alcohol in 85% isolated yield within 20 hours under these conditions, whereas *o*-nitrobenzaldehyde and *p*-anisaldehyde give the corresponding alcohols in yields of 55 and 86%, respectively. 1-Octanal yields 1-octanol in 80% yield after just six hours.⁹¹ Triethoxysilane and diethoxymethylsilane are not as effective as reducing agents as trimethoxysilane. Sodium methoxide, alkali metal ethoxides, and, especially, potassium methoxide also are effective nucleophilic promoters. Lithium and sodium pinacولات are strong promoters that cause the reduction of both aldehydes and ketones.⁹¹

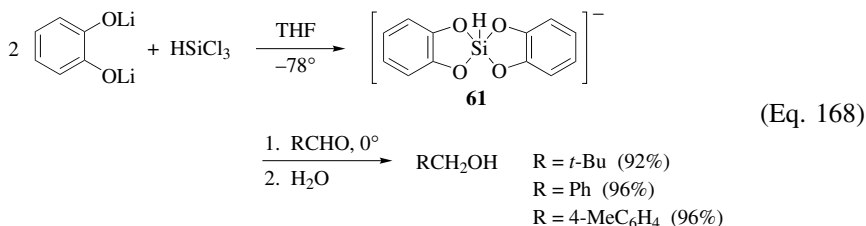


There seems little doubt that the active reducing agents in these kinds of reductions are pentavalent hydridosilicates. In fact, it is possible to produce the stable potassium salts of these species in high yield by reacting equivalent amounts of the appropriate trialkoxysilanes and potassium alkoxides in large amounts of tetrahydrofuran or 1,2-dimethoxyethane (DME) at room temperature (Eq. 166).¹⁰⁷ A variety of alkoxy groups may be used ($\text{R} = \text{Et}$, *i*-Pr, Ph), but neither lithium nor sodium alkoxides are effective in this reaction.¹⁰⁷ Potassium tetraethoxyhydrosilicate shows high reducing properties toward both aldehydes and ketones without the need for added catalysts (Eq. 167).²⁸⁸ It reduces benzaldehyde to benzyl alcohol in 90% yield and 1-pentanal to 1-pentanol in 80% yield following aqueous acid workup.²⁸⁸



A similar reducing system is created by combining dilithium catecholate and trichlorosilane at -78° in tetrahydrofuran. It is speculated that the relatively unstable pentacoordinate bis(1,2-benzenediolato)hydridosilicate (**61**) is formed in situ and that it is this species that can reduce aldehydes and ketones, but not esters, to alcohols when they are added to the reaction mixture at 0° (Eq. 168).⁹³ In a like manner, the dilithium salt of 2,2'-dihydroxybiphenyl, which forms a pentacoordinate intermediate that is stable enough to react at room temperature, can also be used to promote the reduction reaction. The alkoxides of aliphatic diols

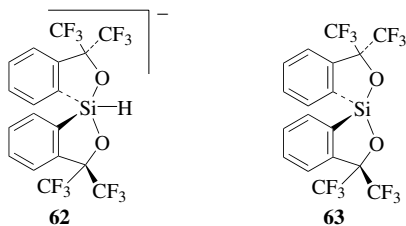
such as 1,2-ethanediol and pinacol are not very effective as ligand promoters in this system and those of simple alcohols are without effect. Use of the dilithium catecholate/trichlorosilane combination gives benzyl alcohol from benzaldehyde in 96% yield within two hours. Substitution of 2,2'-dihydroxybiphenyl for catechol provides a 92% yield of 2,2-dimethylpropanol from 2,2-dimethylpropanal within five hours at room temperature.⁹³



Chemoselectivity between aldehydes and ketones is demonstrated by this method in the competitive reduction of a mixture of pentanal and cyclohexanone. The ratios of primary and secondary alcohols are 75:25 when catechol is used at 0° and 79:21 when 2,2'-dihydroxybiphenyl is used at room temperature. These reagents are not as chemoselective as other reducing agents such as $\text{LiAlH}(\text{O}i\text{Bu})_3$ (87:13) and $\text{LiAlH}(\text{OCe}t_3)_3$ (94:6) at 0°.⁹³

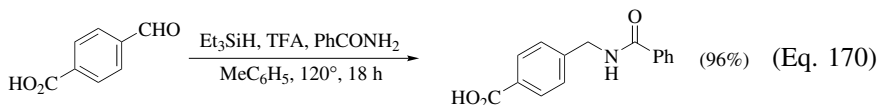
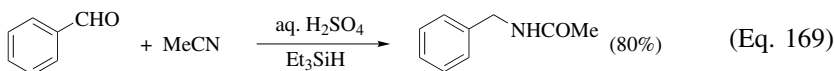
Several types of organosilicon hydrides are effective reducing agents toward carbonyl functions because of valence expansion produced by intramolecular effects. Aryl silyl hydrides with amine functions are especially prone to having the proper configuration to permit such intramolecular valence expansion.^{321,322} The valence expanded silicon hydrides compounds **58**–**60** react spontaneously with both *p*-nitrobenzaldehyde and *p*-anisaldehyde to give, within 0.5 to 3 days, the respective benzyl alcohols in quantitative yields following aqueous acidic workup.³²¹ Under the same conditions, a mixture of α -naphthylphenylsilane and *N,N*-dimethylbenzylamine fails to react even after 17 days.³²¹ It is of interest to note that the silyl hydrides **58**, **59**, and **60** (Eqs. 136 and 137) all have trigonal bipyramidal structures in which the active hydrogens occupy equatorial positions. Compound **58** is such an effective carbonyl reducing agent that it reduces carbon dioxide to formaldehyde via a stable silylformate intermediate.³²³

The 10-*Si*-5-hydridosilicate ion **62** is known in association with lithium,³²³ tetrabutylammonium,¹⁰¹ and bis(phosphoranyl)iminium⁹³ cations. It is synthesized by hydride addition to the 8-*Si*-4-silane **63**, which is derived from hexafluoroacetone.¹⁰¹ Benzaldehyde and related aryl aldehydes are reduced by solutions of **62** in dichloromethane at room temperature¹⁰¹ or in tetrahydrofuran at 0°⁹⁶ within two hours. The alkyl aldehyde, 1-nonanal, is also reduced by **62** in tetrahydrofuran at 0°.⁹⁶ Good to excellent yields of the respective alcohols are obtained following hydrolytic workup. The reactions are not accelerated by addition of excess lithium chloride,⁹⁶ but neutral **63** catalyzes the reaction, apparently through complexation of its silicon center with the carbonyl oxygen prior to delivery of hydride from **62**.¹⁰¹

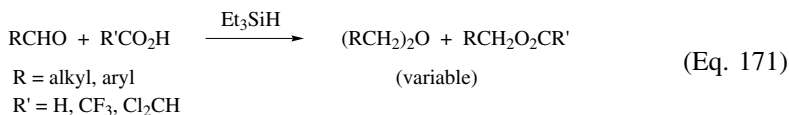


The solid bases CaO and hydroxyapatite catalyze the hydrosilylation of benzaldehyde by triethoxysilane at 90° in yields of 59% and 72% within one and two hours, respectively.^{323,324} These reductions also very likely involve activation by valence expansion of the silicon hydride reagent.

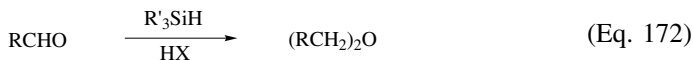
Reductive Amidation of Aldehydes. The reductive amidation of aldehydes using an organosilane as the reducing agent has been realized. Benzaldehyde reacts over a 74-hour period with triethylsilane and acetonitrile in 75% aqueous sulfuric acid at room temperature to produce an 80% isolated yield of *N*-benzylacetamide (Eq. 169).³¹³ Octanal fails to react under the same conditions.³¹³ Reductive amidation of aldehydes also occurs with the reagent combination Et₃SiH/TFA/primary amide (Eq. 170).³²⁶



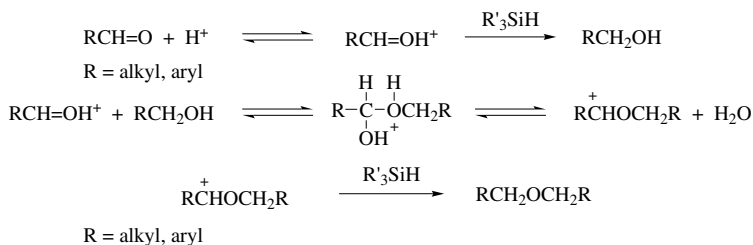
Reductive Esterification. Aldehydes can give ester products when treated with combinations of organosilicon hydrides and carboxylic acids that have appreciable basicity. Benzaldehyde gives a product mixture consisting of 12% dibenzyl ether and 88% of benzyl formate when it is treated for 8 hours at room temperature with a slight excess of triethylsilane in formic acid.³¹³ *p*-Nitrobenzaldehyde produces 33% bis(*p*-nitrobenzyl) ether and 66% of *p*-nitrobenzyl trifluoroacetate when it reacts with Et₃SiH/TFA for 5 hours at room temperature. Other aldehydes give small, variable amounts of esters under similar reaction conditions. Although this general approach to the synthesis of esters from aldehydes is an attractive one, it appears not yet to be optimized for maximum synthetic utility because of the frequent formation of considerable amounts of ether products (Eq. 171).³¹³



Reductive Etherification. As indicated earlier, aldehydes as well as ketones often give very good yields of ethers when they are treated with Brønsted acids or other electrophilic species in the presence of organosilicon hydrides (Eq. 172). In the absence of added alcohols, symmetrical ethers are obtained.



When alcohols are added to the reaction mixture, unsymmetrical ether products may be obtained. Starting with a mixture of aldehydes can also give rise to the formation of unsymmetrical ethers. These ether products are formed under conditions different from those used in the formation of ethers directly from alcohols. Thus, it is postulated that the reaction sequence that leads from the carbonyl substrate to the ether involves the intermediate formation of hemiacetals, acetals, or their protonated forms and alkoxy-carbenium ions, which are intercepted and reduced to the final ether products by the organosilicon hydrides present in the reaction mix. The probable mechanistic scheme that is followed when Brønsted acids are present is outlined in Scheme 2.^{311,327,328}



Scheme 2

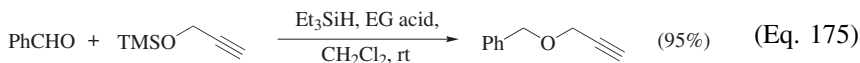
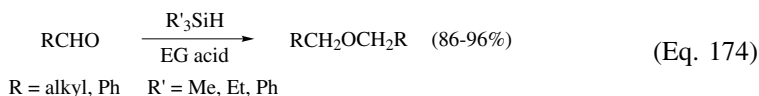
Reduction of aldehydes to symmetrical ethers can be accomplished in good to excellent yields with $\text{Et}_3\text{SiH}/\text{Ph}_3\text{C}^+ \text{ClO}_4^-$,³²⁹ $\text{Et}_3\text{SiH}/\text{ZnCl}_2$,³³⁰ $\text{Me}_2\text{ClSiH}/\text{In}(\text{OH})_3$,³³¹ $\text{Et}_3\text{SiH}/\text{BiCl}_3$,³³² $(\text{HMe}_2\text{Si})_2\text{O}/\text{TMSOTf}$ (or TMSCl/NaI),³¹⁴ Et_3SiH (or PhMe_2SiH)/ Bu_4NClO_4 ,³³³ $\text{Et}_3\text{SiH}/\text{TMSOTf}$,³³⁴ $\text{Et}_3\text{SiH}/\text{H}_2\text{SO}_4$,³²⁸ and $\text{Et}_3\text{SiH}/\text{TFA}$.³¹³ The reaction of 1.4 equivalents of triethylsilane with two equivalents of trifluoroacetic acid rapidly reduces benzaldehyde to dibenzyl ether in 80% yield at temperatures below 40°. ³¹¹ Similar treatment of *n*-butanal with two equivalents of triethylsilane and three equivalents of trifluoroacetic acid produces di-*n*-butyl ether in a more modest 37% yield. ³¹¹ Variations of these simple reaction conditions permit greater yields of desired ether products to be obtained. For example, 1-heptanal reacts with a 10 mol% excess of triethylsilane to give a 90% yield of di-*n*-heptyl ether within 45 minutes at room temperature when the reaction is run in a twenty-fold excess of trifluoroacetic acid acting as solvent. ³¹³ With the exception of *p*-nitrobenzaldehyde, which gives only a 33% yield of the symmetrical ether (the remainder is converted into *p*-nitrobenzyl trifluoroacetate), other representative aryl aldehydes normally give yields of symmetrical ethers on the order of 80% or greater. ³¹³

Unsymmetrical ethers may be produced from the acid-promoted reactions of aldehydes and organosilicon hydrides when alcohols are introduced into the reaction medium (Eq. 173).^{327,328} An orthoester can be used in place of the alcohol in this transformation.^{327,335} A cyclic version of this conversion is reported.³³⁶ Treatment of a mixture of benzaldehyde and a 10 mol% excess of triethylsilane with methanol and sulfuric, trifluoroacetic, or trichloroacetic acid produces benzyl methyl ether in 85–87% yields.³²⁸ Changing the alcohol to ethanol, 1-propanol, 2-propanol, or 1-heptanol gives the corresponding unsymmetrical benzyl alkyl ethers in 45–87% yield with little or no side products.³²⁸ A notable exception is the tertiary alcohol 2-methyl-2-propanol, which requires 24 hours.³²⁸ 1-Heptanal gives an 87% yield of *n*-heptyl methyl ether with added methanol and a 49% yield of benzyl *n*-heptyl ether with added benzyl alcohol under similar conditions.³²⁸



The yield of ethyl *n*-pentyl ether formed from the reduction of 1-pentanal by $\text{Et}_3\text{SiH/TFA}$ in ethanol is 57% after 6–8 hours at 50–60°. ³²⁷ The yield of product increases to 72% when one equivalent of ethyl orthoformate and some anhydrous hydrogen chloride are added to the reaction medium.³²⁷ Presumably, this reduces the amount of free water in the reaction medium.

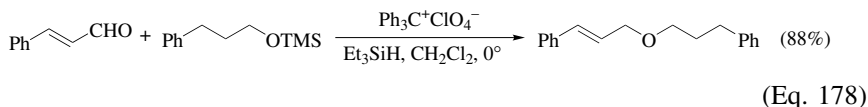
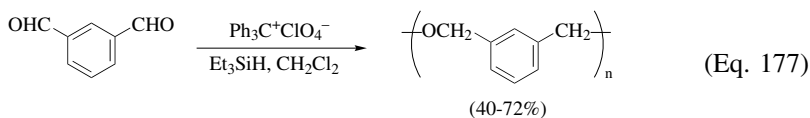
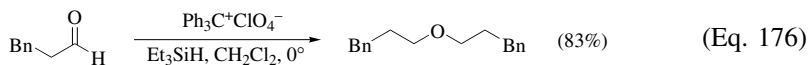
An interesting and effective variation of this general synthetic approach uses electrogenerated acid (EG acid) to assist in the formation of ethers from aldehydes.³³³ This method permits the synthesis of both symmetrical and unsymmetrical ethers. The experiments are conducted using platinum electrodes in a simple undivided cell. A mixture of aldehyde and a 20 mol% excess of either triethylsilane or dimethylphenylsilane in dichloromethane solvent containing lithium perchlorate and tetra-*n*-butylammonium perchlorate is electrolyzed by the passage of small amounts of current (0.04–0.45 Faradays/mol) to give symmetrical ethers (Eq. 174). In this way, both dibenzyl and dialkyl ethers may be produced in excellent yields (86–96%).³³³ Unsymmetrical ethers are produced in 50–99% yields when alkoxytrimethylsilanes are added to the reaction mixture (Eq. 175).³³³ The alkoxy groups can include allyl, propargyl, and 3-phenylpropyl moieties. Phenol trimethylsilyl ether is ineffective in producing phenyl ethers.³³³



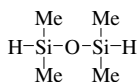
Various chemical species with Lewis acid properties are also effective in promoting the direct conversion of aldehydes into ethers by organosilicon hydrides.

They offer the advantage that reductions can be effected under conditions that permit the conversion of substrates that may be adversely sensitive to the presence of strong Brønsted acids. For example, in the presence of a 10% excess of triethylsilane, addition of one-half equivalent of boron trifluoride etherate to octanal results, within one hour, in the formation of a 66% yield of dioctyl ether after a basic hydrolytic workup. Benzaldehyde provides a 75% yield of dibenzyl ether under the same reaction conditions. The remainder of the mass is found as the respective alcohol.⁷⁰ Zinc chloride is also capable of catalyzing this reaction. With its use, simple alkyl aldehydes are converted into the symmetrical ethers in about 50% yields.³³⁰

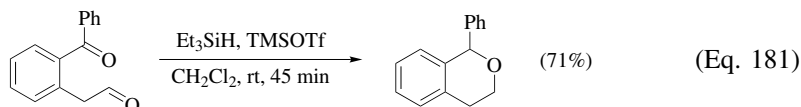
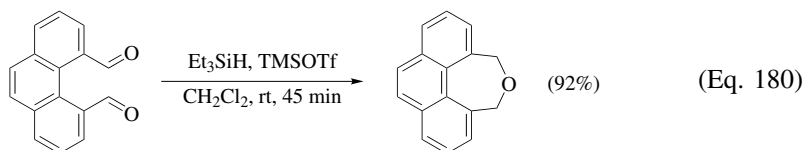
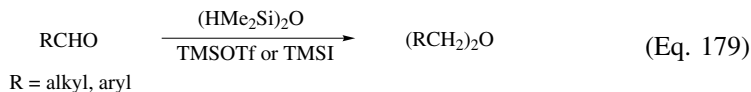
Superior yields of ethers from aldehydes are obtained by the use of several other electrophilic species. The addition of 5 mol% of trityl perchlorate to a mixture of triethylsilane and 3-phenylpropanal in dichloromethane at 0° produces an 83% yield of bis-(3-phenylpropyl) ether within 10 minutes (Eq. 176).³²⁹ Reductive polycondensation of isophthalaldehyde occurs with two equivalents of triethylsilane in the presence of 10 mol% of trityl perchlorate to give 40–72% yields of polyether with average molecular weights ranging from 6,500 to 11,400 daltons (Eq. 177).³³⁷ Addition of one equivalent of an alkoxytrimethylsilane to the reaction mixture produces unsymmetrical ethers in good to excellent yields. Thus, a mixture of (*E*)-cinnamaldehyde, 3-phenylpropoxytrimethylsilane, and triethylsilane in dichloromethane reacts under the influence of a catalytic amount of trityl perchlorate to give the unsymmetrical ether in 88% yield (Eq. 178).³²⁹



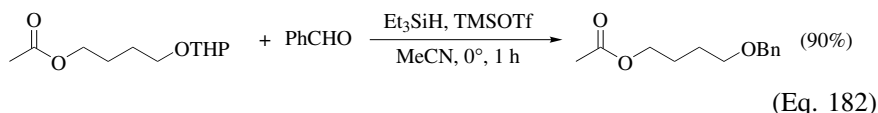
The use of trimethylsilyl-based electrophilic catalysts with organosilicon hydrides also promotes the conversion of aldehydes into ethers and avoids the need to employ the potentially hazardous trityl perchlorate salt.^{314,334,338} One reagent pair that is particularly effective in the reductive conversion of aldehydes into symmetrical ethers is a catalytic amount of trimethylsilyl triflate combined with either trimethylsilane, triethylsilane, PMHS,³³⁴ or 1,1,3,3-tetramethyldisiloxane (TMDO, **64**) as the reducing agent (Eq. 179).³¹⁴ Either



dichloromethane or benzene can be used as the solvent. The reactions occur at temperatures ranging from 0° to 80°. These conditions produce symmetrical ethers from both aromatic and aliphatic aldehydes in yields frequently exceeding 90%. Aromatic aldehydes tend to give minor amounts of benzyl alcohols as by-products.³³⁴ The synthesis of cyclic ethers from dialdehydes or keto aldehydes is also possible (Eqs. 180 and 181).³³⁹

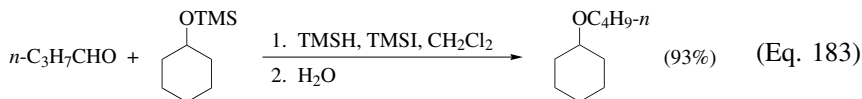


The formation of unsymmetrical ethers from the reduction of aldehydes in the presence of tetrahydropyran (THP) ethers is reported (Eq. 182).³⁴⁰

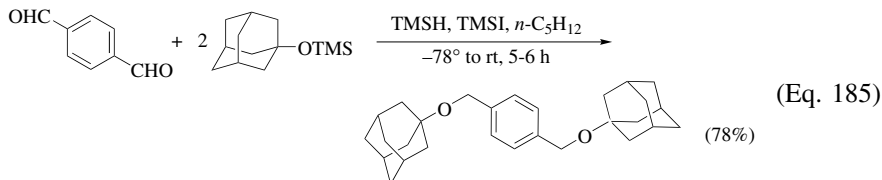
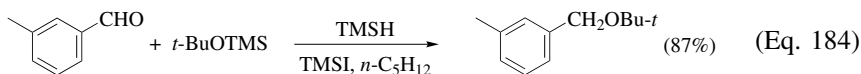


Trimethylsilyl iodide can be substituted for the trimethylsilyl triflate catalyst in the reactions of aliphatic aldehydes. TMSI can be generated conveniently in situ either from trimethylsilyl chloride and sodium iodide in acetonitrile³¹⁴ or from hexamethyldisilane and iodine in dichloromethane³³⁴ or pentane.³³⁸ It is noted that neither triisopropylsilane nor PMHS is an effective reducing agent for this purpose when used with TMSI under these conditions.^{314,334}

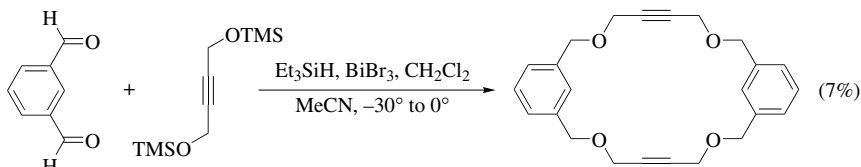
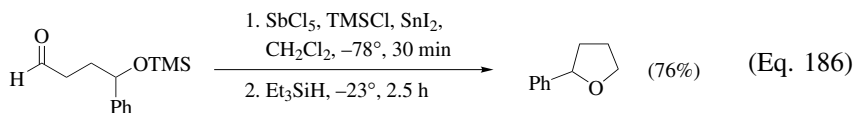
Equivalent amounts of aldehydes and alkoxytrimethylsilanes react to form unsymmetrical ethers in near quantitative yields in the presence of either trimethylsilane or triethylsilane and catalytic amounts (ca. 10 mol%) of TMSI in dichloromethane.^{329,333,334,341} The procedure is particularly convenient experimentally when trimethylsilane is used with TMSI because the catalyst provides its own color indicator for the reduction step (color change from deep violet to vivid red-gold) and the only silicon-containing product following aqueous workup is the volatile hexamethyldisiloxane (bp 99–100°). It is possible to introduce trimethylsilane (bp 7°) either as a previously prepared solution in dichloromethane or by bubbling it directly into the reaction mixture. Cyclohexyloxytrimethylsilane and *n*-butanal react by this method to give a 93% isolated yield of *n*-butyl cyclohexyl ether (Eq. 183).³³⁴



Trimethylsilane in pentane is a particularly good system for the TMSI-catalyzed reductive coupling of tertiary alkoxytrimethylsilanes with aldehydes to form sterically crowded tertiary-primary ethers.³³⁷ In this way, 1-(*tert*-butoxymethyl)-3-methylbenzene is formed in 87% yield (Eq. 184).³³⁸ Reaction of terephthalaldehyde with two equivalents of the trimethylsilyl ether of 1-adamantanol under these conditions leads to a good yield of the diadamantyl ether of 1,4-benzenedimethanol (Eq. 185).³³⁸



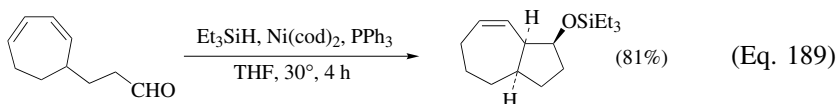
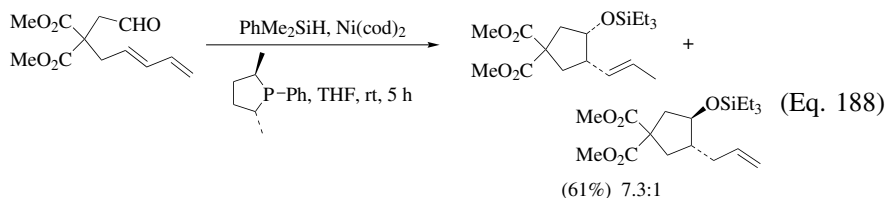
Cyclic ethers can also be formed in a fashion similar to that of the reactions described previously (Eq. 186),^{306,342} and also result from the reductive etherification of bis(trimethylsilylated) diols and dialdehydes (Eq. 187).³⁴³



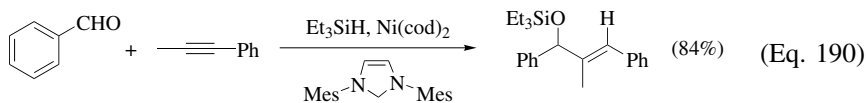
(Eq. 187)

The reductive silylation of aldehydes provides a one-step route to silyl ethers. This is accomplished with the reagent combinations $\text{PhMe}_2\text{SiH/CuH(PPh}_3\text{)}$,³¹⁷ $\text{Et}_3\text{SiH/ZnCl}_2$ (or SnCl_2 or NiCl_2),³⁴³ $\text{Ph}_2\text{SiH}_2/\text{CsF}$ (or KF , BnMe_3 , NF , KO_2CH),^{75,319} $\text{Et}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$,^{115,281} $\text{PhMe}_2\text{SiH/CsF}$,^{320,345-347} and $\text{Et}_3\text{SiH/TBAF}$.⁷⁶ Montmorillonite clay that has been subjected to ion exchange with ferric ion catalyzes the hydrosilylation of benzaldehyde with triethylsilane to give benzyl triethylsilyl ether in 79% yield.^{324,325}

Various non-conjugated diene aldehydes react with $\text{Et}_3\text{SiH}/\text{Ni}(\text{cod})_2/\text{PPh}_3$ to give O-triethylsilylated cycloalkanols in low to high yields. Acyclic dienes can lead to the silylated cycloalkanols in moderate yields with the proper catalyst (Eq. 188).³⁴⁸ Bicyclic systems are also generated by this methodology (Eq. 189).³⁴⁹

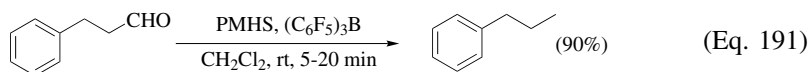


$\text{Et}_3\text{SiH}/\text{Ni}(\text{cod})_2$ brings about the reaction of an aldehyde and an alkyne to provide the silylated allyl alcohol (Eq. 190).³⁵⁰ The reaction also occurs in an intramolecular mode.



Reduction to Alkanes. Carbonyl groups can be reductively deoxygenated to methylene functions if both of the two steps represented by Eqs. 1 and 2 proceed to completion. With aldehydes, this process leads to the transformation of the CHO group into a CH_3 group.

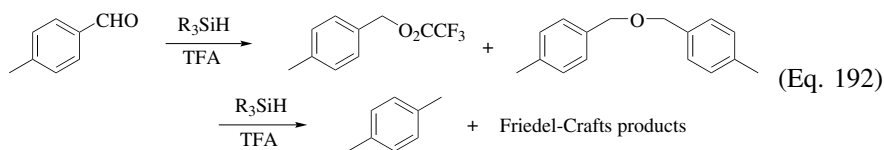
The relative instability of primary alkyl carbenium ions in the condensed phase and the weak intrinsic nucleophilicity of organosilicon hydrides are the reasons that primary alkyl alcohols are not reduced to hydrocarbons. For these same reasons, aliphatic aldehydes do not undergo complete deoxygenation to methyl-terminated hydrocarbons when treated with acids and organosilicon hydrides under usual laboratory conditions. In contrast, many aryl aldehydes can be transformed into methylarenes by this method. Since the organosilane reduction of benzyl alcohols to the corresponding toluene derivatives is known, it is not surprising that the reduction of an aryl aldehyde to a toluene is possible. This transformation has been carried out with $\text{Et}_3\text{SiH}/\text{TFA}$,^{69,351,352} $(\text{EtO})_3\text{SiH}$, and Et_3SiH with various catalysts,³⁵³ $\text{Et}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$,²⁸¹ $\text{PMHS}/\text{Pd}/\text{C}$,³¹⁶ and $\text{PMHS}/(\text{C}_6\text{F}_5)_3\text{B}$.³⁵⁴ The last combination also reduces alkyl aldehydes to the corresponding alkanes (Eq. 191).^{281,282,354}



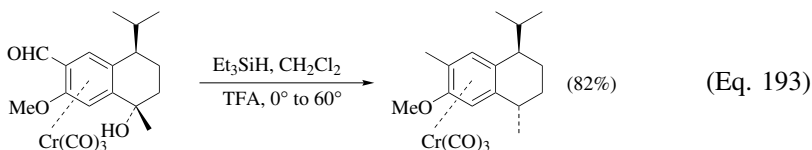
Trifluoroacetic acid solutions of benzaldehydes having electron-donating ring substituents form the corresponding methyl arenes when at least two equivalents of an organosilicon hydride are added to the solution at room temperature. The reaction conditions permit preservation of the integrity of functions such as halogen, alkoxy, carboxylate, cyano, and nitro. There is little difference in the reducing abilities of triethylsilane, tri-*n*-propylsilane, and tri-*n*-hexylsilane in these reactions. Thus, the silane reducing agent can be chosen that best suits purification of the desired product. Basic aqueous workup converts the silicon reaction products derived from the organosilicon hydride into the corresponding silanols and disiloxanes, which may be removed from the desired reduction products by simple distillation.⁶⁹

Benzaldehyde itself forms no toluene; only dibenzyl ether and benzyl trifluoroacetate are formed. Triethylsilane (2.2 equivalents) causes the transformation of *p*-anisaldehyde into *p*-methylanisole in 76% yield after only 30 minutes. Use of a three-fold excess of dimethylphenylsilane in place of the triethylsilane results in a slight improvement in yield to 83% after 45 minutes.⁶⁹

Similar treatment of a trifluoroacetic acid solution of *p*-tolualdehyde with triethylsilane gives only a 20% yield of *p*-xylene after 11 hours reaction time followed by basic workup. Use of 2.5 equivalents of dimethylphenylsilane enhances the yield to 52% after only 15 minutes. This reaction proceeds stepwise through the formation of a mixture of the trifluoroacetate and the symmetrical ether. These intermediates slowly form the desired *p*-xylene product along with Friedel-Crafts side products under the reaction conditions (Eq. 192).⁷³ Addition of co-solvents such as carbon tetrachloride or nitromethane helps reduce the amount of the Friedel-Crafts side products.⁷³

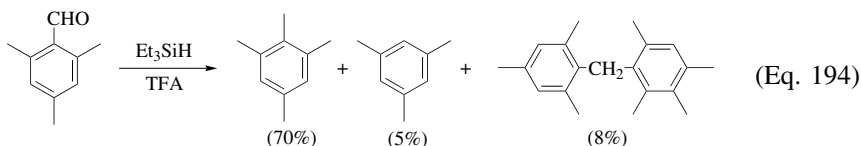


Treatment of a polyfunctional chromium-tricarbonyl-complexed hydroxy aldehyde with an excess of $\text{Et}_3\text{SiH}/\text{TFA}$ for 4.5 hours gives an 82% yield of fully reduced product with both the formyl and hydroxy groups completely and selectively reduced (Eq. 193).³⁵²

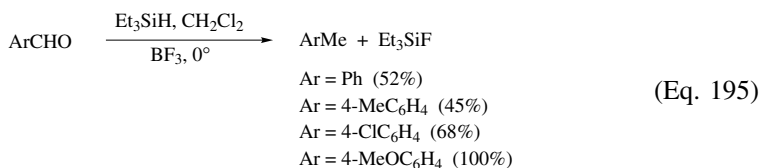


The sequence of reagent and substrate addition can be quite important in these reactions. For example, a trifluoroacetic acid solution of 2,4,6-trimethylbenzaldehyde forms isodurene in 98% yield within 15 minutes when 2.2 equivalents of triethylsilane are added to the reaction mixture at room temperature.⁶⁹ In

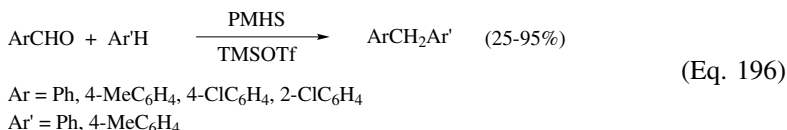
contrast, when trifluoroacetic acid is added to a stirred solution of triethylsilane and 2,4,6-trimethylbenzaldehyde, isodurene is formed in only 70% yield after basic aqueous workup. Minor side products under these reaction conditions are mesitylene (formed via acid-catalyzed decarbonylation of the aldehyde) and the Friedel-Crafts product 2,4,6,2',3',4',6'-heptamethyldiphenylmethane (Eq. 194).³¹¹



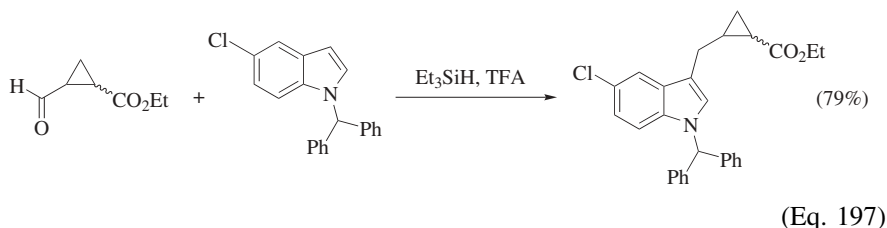
The $\text{Et}_3\text{SiH}/\text{BF}_3 \cdot \text{OEt}_2$ combination fails to cause complete deoxidative reduction of aldehydes, forming instead mixtures of primary alcohols and symmetrical ethers.⁷⁴ By contrast, aryl aldehydes lacking electron-withdrawing ring substituents, when reacted in dichloromethane with at least two equivalents of triethylsilane and gaseous boron trifluoride at 0° , form the corresponding methylarenes within a few minutes (Eq. 195).¹ Even benzaldehyde produces a 52% yield of toluene by this method when 18 equivalents of triethylsilane are added to suppress formation of Friedel-Crafts oligomers. The method offers the advantage that fluorotriethylsilane is formed, which is volatile and is easily separated from the desired organic products.¹



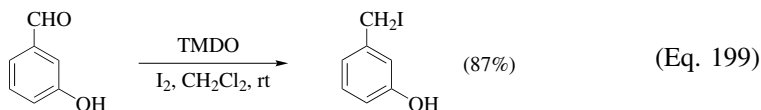
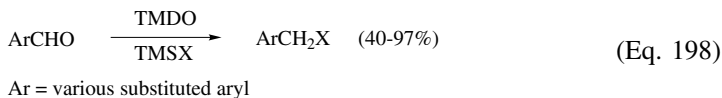
If Friedel-Crafts products are desired, a clever method exists for the direct conversion of aryl aldehydes into diarylmethanes. Reaction of a mixture of an aromatic aldehyde and a catalytic amount of trimethylsilyl trifluoromethanesulfonate and excess polymethylhydrosiloxane in either benzene or toluene at reflux results in the formation of the respective arylphenyl or tolylmethanes in reasonably good yields within 1–3 hours (Eq. 196).³¹⁴ Thus, benzaldehyde reacts in refluxing benzene containing a few drops of TMSOTf and excess PMHS to give diphenylmethane in 92% yield within two hours and in refluxing toluene within one hour to give a 95% yield of a mixture of phenyl-*p*-tolylmethane and phenyl-*o*-tolylmethane in a 70:30 ratio. *p*-Tolualdehyde gives a 60% yield of phenyl-*p*-tolylmethane when heated at reflux in benzene for 2.5 hours and an 80% yield of di-*p*-tolylmethane and *p*-tolyl-*o*-tolylmethane in a 90:10 ratio when heated at reflux in toluene for 30 minutes. *o*-Chlorobenzaldehyde gives a mixture of 25% phenyl-*o*-chlorophenylmethane and 55% of bis(*o*-chlorophenyl)ether, and *p*-chlorobenzaldehyde gives a 65% yield of a mixture of phenyl-*p*-chlorophenylmethane and bis(*p*-chlorophenyl)ether in a 75:25 ratio when heated at reflux in benzene for 3 hours.³¹⁴



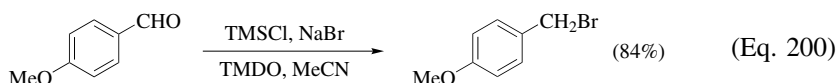
The TFA-catalyzed triethylsilane reductive condensation of an aldehyde with indoles provides a convenient route to 3-substituted indoles in modest to good yields (Eq. 197).³⁵⁵



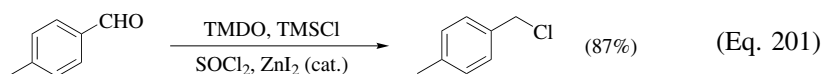
Reduction to Methylene Halides. Treatment of aryl aldehydes with selected organosilicon hydrides and an appropriate trimethylsilyl halide produces benzyl chlorides, bromides, and iodides directly in good to excellent yields by reductive halogenation (Eq. 198). This protocol offers the advantage of being simple and leading only to the monohalo derivatives. The method is specific for the carbonyl group of both aryl ketones and aldehydes and preserves the integrity of many other groups (e.g. ring halogen, alkyl, alkoxy, cyano, nitro, hydroxy, ester) that may be found in polyfunctional compounds. Alkyl aldehydes form symmetrical ethers instead of halides under these reaction conditions.^{314,356,357} Several variations of this general method exist. In the most straightforward approach for synthesizing iodides, the addition of an external trimethylsilyl reagent is not required. Aromatic aldehydes normally react within minutes at room temperature with iodine and TMDO in dichloromethane solution to produce benzyl iodides in high yields (66–87%) (Eq. 199). A reactive silyl iodide is believed to be formed in situ from tetramethyldisiloxane and iodine under these conditions. The reaction is not limited to aryl rings with only electron-donating groups; chloro-, hydroxy-, alkyl-, alkoxy-, cyano-, and carboalkoxy-substituted rings all undergo the transformation.³⁵⁷ The same transformation can be carried out with diiodosilane.³⁵⁸



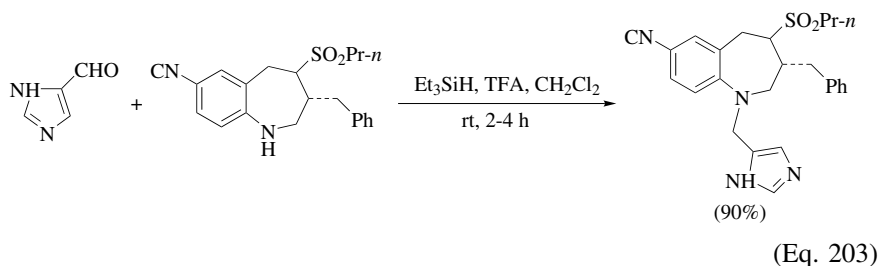
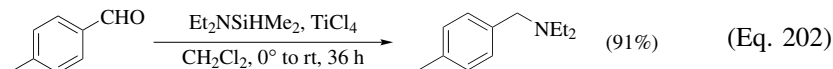
Another variation of this method involves the treatment of an acetonitrile solution of the aryl aldehyde, trimethylsilyl chloride, and either sodium iodide, if iodide products are desired, or lithium bromide, if bromide products are desired, with TMDO. After an appropriate reaction time (5–195 minutes) at a temperature in the range of -70° to 80° , the upper siloxane layer is removed and the benzyl iodide or bromide product is isolated from the remaining lower portion after precipitation of the inorganic salts by addition of dichloromethane. For example, *p*-anisaldehyde reacts to form *p*-methoxybenzyl bromide in 84% isolated yield under these conditions (Eq. 200).^{314,356}



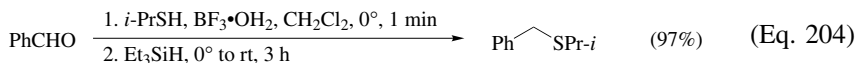
In the preparation of iodides, but not bromides, PMHS may be substituted for the TMDO. Chlorides can be obtained if thionyl chloride and zinc iodide are added to suppress the formation of symmetrical ethers.³¹⁴ An example of this type of reductive chlorination is shown by the TMDO-mediated conversion of *p*-tolualdehyde into *p*-methylbenzyl chloride (Eq. 201).³¹³ To obtain chlorides from aldehydes having electron-withdrawing groups such as nitro or carbomethoxy, the initial reaction is first carried out at -70° and the mixture is then heated to reflux in order to reduce the formation of symmetrical ether by-products. Zinc chloride is substituted for zinc iodide for the synthesis of chlorides of substrates with electron-donating groups such as methoxy and hydroxy.³¹⁴



Reductive Amination. Reaction of an aminohydrodimethylsilane with aldehydes in the presence of a Lewis acid catalyst gives the corresponding amine in good to high yields (Eq. 202).³⁵⁹ The use of an $\text{Et}_3\text{SiH/TFA/amine}$ reagent combination also leads to the reductive amination of aldehydes (Eq. 203).³⁶⁰ Comparable reductive aminations of aldehydes are possible in moderate yields with $\text{PhSiH}_3/\text{Bu}_2\text{SnCl}_2/\text{amine}$,^{361,362} and in good yields with $\text{PMHS/TiCl}_4/\text{amine}$ ³⁶³ or with $\text{amine/Cl}_3\text{SiH}$.³⁶⁴



Reductive Thiolation. Treatment of aldehydes with triethylsilane, thiols, and boron trifluoride monohydrate^{6,217} yields sulfides in a one-flask process. For example, this method gives a 97% yield of benzyl isopropyl sulfide from benzaldehyde and 2-propanethiol (Eq. 204).³⁶⁵

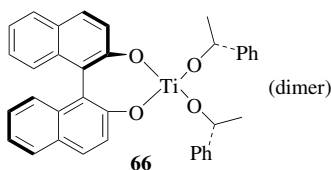
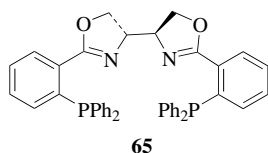


Reduction of Ketones

The selective organosilane reduction of ketone functions can be effected in the presence of a number of other functional groups including epoxides,^{320,366} ketals,^{86,367} thioketals,³⁶⁸ other ketones,^{369,370} β -lactams,³⁷¹ alkynes,³⁷² esters,^{79,80,83,84,87,320,373,374} α -bromides,^{76,80,83} amides^{80,83,84,86,276,320,375} ureas,^{84,276} trifluoroacetamides,^{83,376} sulfonamides,^{83,86} and nitro groups.⁸⁰

Reduction to Alcohols. The organosilane-mediated reduction of ketones to secondary alcohols has been shown to occur under a wide variety of conditions. Only those reactions that are of high yield and of a more practical nature are mentioned here. As with aldehydes, ketones do not normally react spontaneously with organosilicon hydrides to form alcohols. The exceptional behavior of some organocobalt cluster complex carbonyl compounds was noted previously. Introduction of acids or other electrophilic species that are capable of coordination with the carbonyl oxygen enables reduction to occur by transfer of silyl hydride to the polarized carbonyl carbon (Eq. 2). This permits facile, chemoselective reduction of many ketones to alcohols.

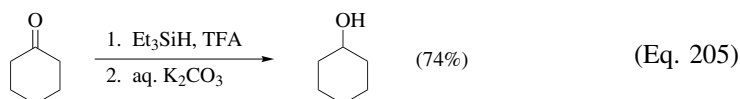
Certain catalysts promote the reduction of ketones with organosilanes. The reduction of acetophenone with Et_3SiH is catalyzed by the diphosphine **65** and gives only a small amount of overreduction to ethylbenzene.³⁷⁷ Aryl alkyl enones and ynones are reduced to the corresponding alcohols with triethoxysilane and the titanium-based catalyst **66**.³⁷⁸ Trichlorosilane reduces acetophenone in 90% yield with *N*-formylpyrrolidine catalysis.³⁷⁹



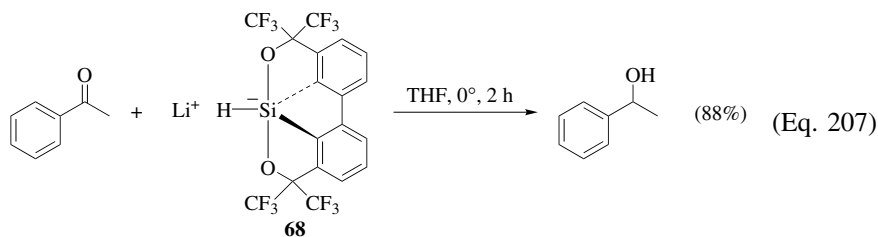
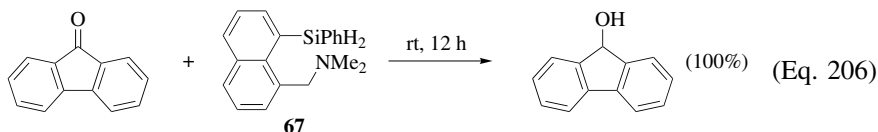
Promotion by Acid. The same range of Lewis and Brønsted acids that promote the silane reduction of aldehydes can be used for the reduction of ketones. These acid-catalyzed reductions appear to proceed by direct hydride transfer rather than by a single-electron transfer mechanism.³⁸⁰ Similar to the case of aldehydes, the silane reductions of ketones promoted by Brønsted acids rarely give clean yields of alcohols when conducted under anhydrous conditions. Instead, mixtures of alcohols, esters, and silyl ethers often result.^{313,381} The reagent combination of $\text{Et}_3\text{SiH}/\text{HCl}$ (or H_2SO_4) gives good yields of the alcohol, although

by-products of the sym-ether among others can complicate the reduction.³¹³ Use of zinc chloride to promote organosilicon hydride reduction of ketones to siloxanes that can be hydrolyzed to alcohols is well known. It is one of the first Lewis acid catalysts reported to be useful for this purpose,^{382,383} although others are known.³⁸⁴ The combination of $\text{Et}_3\text{SiH}/\text{TFA}/\text{NH}_4\text{F}$ provides a good yield of the alcohol with some ether formation.¹³⁵ High yields of the alcohol from both aryl and alkyl ketones are realized by the $\text{HMDS}/(\text{AcOBu}_2\text{Sn})_2\text{O}$ ³¹⁶ and $\text{HMDS}/\text{Sn}(\text{OTf})_2$ ³⁸⁵ reagent combinations. The $\text{Et}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$ combination cleanly reduces aryl ketones to the substituted benzyl alcohols.¹¹⁶

Under certain conditions, the trifluoroacetic acid catalyzed reduction of ketones can result in reductive esterification to form the trifluoroacetate of the alcohol. These reactions are usually accompanied by the formation of side products, which can include the alcohol, alkenes resulting from dehydration, ethers, and methylene compounds from over-reduction.^{68,70,207,208,313,386} These mixtures may be converted into alcohol products if hydrolysis is employed as part of the reaction workup. An example is the reduction of cyclohexanone to cyclohexanol in 74% yield when treated with a two-fold excess of both trifluoroacetic acid and triethylsilane for 24 hours at 55° and followed by hydrolytic workup (Eq. 205).²⁰³

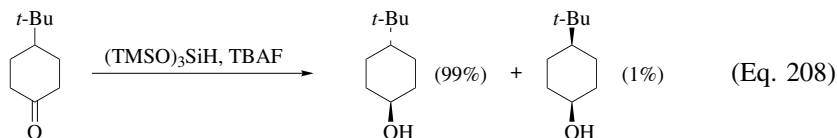


Promotion by Valence Expansion. As in reactions of aldehydes, addition of nucleophilic substances to mixtures of ketones and organosilicon hydrides promotes reduction of the carbonyl group as depicted in Eq. 6. Ketones are conveniently reduced in high yields with reagent combinations of $(\text{EtO})_3\text{SiH}$ or $\text{Me}(\text{EtO})_2\text{SiH}$ and KF (or CsF).⁸⁰ The pentacoordinate silane **67** itself reduces ketones in high yields (Eq. 206).⁸⁴ In a somewhat similar approach, the lithium salt of silicate **68** is a good reducing agent for ketones (Eq. 207).⁹⁶ Other hydridosilicates are known to similarly reduce ketones.⁹³

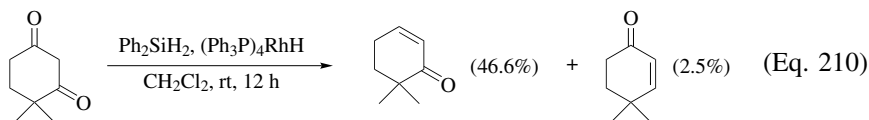
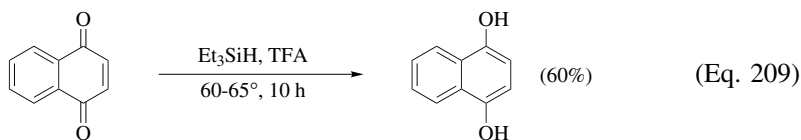


The PMHS/TBAF system provides both an excellent and practical approach to the reduction of aryl ketones to the benzyl alcohols.²⁷⁸ Similarly, the PMHS/Triton[®]B combination gives high yields of the benzyl alcohols.²⁷⁸

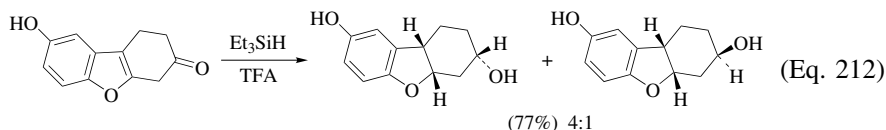
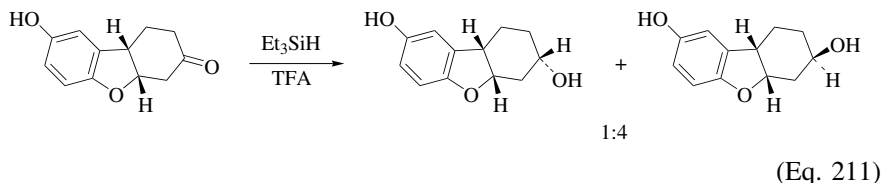
Diastereoselective Reductions. The diastereoselectivity of organosilane reductions of ketones has been the topic of a number of studies. Extensive studies of the Brønsted acid promoted reductions of alkyl-substituted cyclohexanones by mono-, di-, and trialkylsilanes show that chain branching and other steric features of both the silane and the carbonyl substrate can be important factors in determining the isomeric compositions of reduction product mixtures.^{68,381,384,386} In general, the reduction of various substituted cyclohexanones does not show effective diastereoselectivity even when very sterically hindered silanes such as Ph_3SiH ^{387,388} or $(t\text{-Bu})_3\text{SiH}$ ³⁸⁶ are employed. A quite good system is a silane under Triton[®]B or TBAF catalysis.²⁷⁸ The best system for the trans-selective reduction of 4-*tert*-butylcyclohexanone is the sterically encumbered $(\text{TMSO})_3\text{SiH}$ /TBAF (Eq. 208).²⁷⁸ This system is not successful in the stereoselective reduction of 2-methylcyclohexanone, giving a *cis*:*trans* selectivity of 18:82, although 3-methylcyclohexanone gives a *cis*:*trans* ratio of 7:93 and a high (>90%) yield of 3-methylcyclohexanol. The combination of PMHD/dibutylacetoxytin oxide (DBATO) reduces 4-*tert*-butylcyclohexanone exclusively to *trans*-4-*tert*-butylcyclohexanol.³¹⁶ The active reducing agent in this system is likely a tin hydride species. A system of Ph_2MeSiH (or Ph_3SiH)/TBAF/HMPA reduces 2-methylcyclohexanone in a *cis*:*trans* ratio of 95:5.³²⁰ Only *cis*-2-methylcyclohexanol is isolated from the reduction of 2-methylcyclohexanone with $\text{Ph}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$.¹¹⁶ Other systems give only moderate selectivities in the reduction of substituted cyclohexanones.^{70,79,93,116,278,313,367,381,382,384,386,389–392}



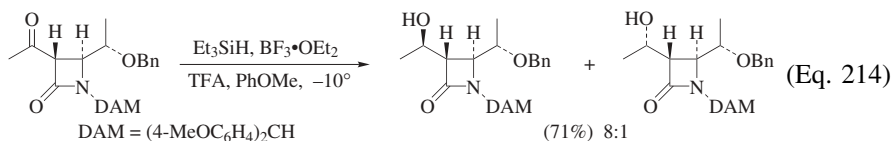
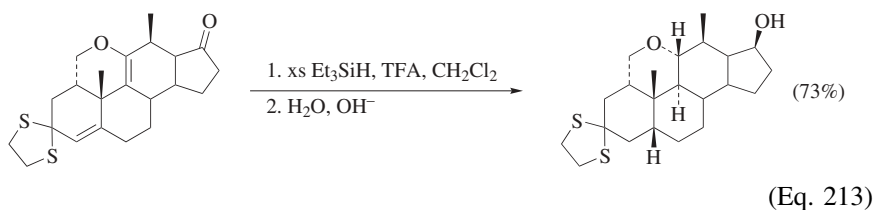
Naphthoquinone is reduced to 1,2,3,4-tetrahydronaphthalene with Et_3SiH /TFA in 60% yield.³⁹³ Quinones can be reduced to hydroquinones in good yields with hydrosiloxanes such as TMDO with iodide present (Eq. 209).^{314,316,357} The reductive dehydration of a 1,3-diketone leads to an enone (Eq. 210).³⁷⁴



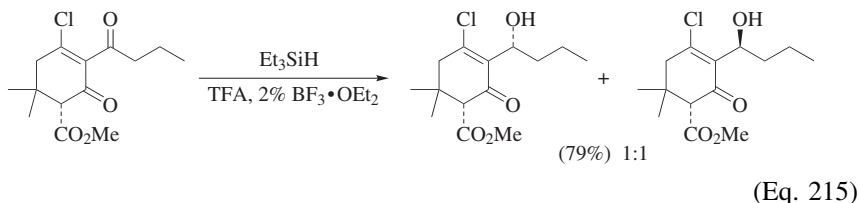
Reduction of the ketone carbonyl of *cis*-1,2,3,4,4a,9b-hexahydro-8-hydroxydibenzofuran-3-one with trifluoroacetic acid and triethylsilane at 0° produces a mixture of the α - and β -isomers of the C3 alcohol with an $\alpha : \beta$ ratio of 1:4 (Eq. 211).³⁹⁴ This result can be compared with the isomer ratio of 100:1 that results when sodium borohydride is used as the reducing agent.³⁹⁴ The same *cis* pair of alcohol isomers is formed in 77% combined yield, but in a reversed ratio of $\alpha : \beta = 4:1$, when the less saturated tetrahydrodibenzofuran analog is used as the substrate (Eq. 212).³⁹⁴



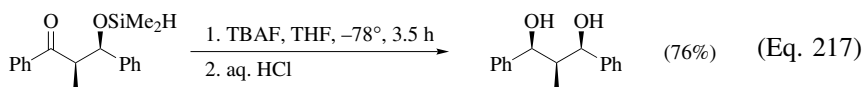
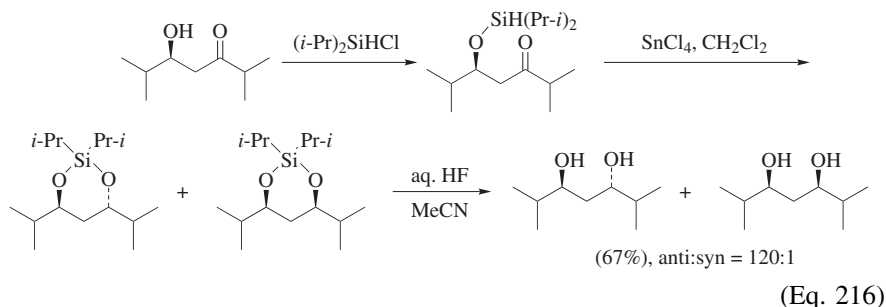
Treatment of a pentacyclic 1 α ,11-(2-oxethano) thioketal steroid with excess Et₃SiH/TFA causes reduction of the carbon-carbon double bonds as well as the 17-carbonyl group to give a single reaction product (Eq. 213).³⁶⁸ Other work utilizes trifluoroacetic acid, triethylsilane, and anisole in the presence of a catalytic amount of boron trifluoride etherate to reduce the acetyl carbonyl of a 3-acetyl-2-azetidinone derivative with a dr of 8:1 (Eq. 214).³⁹⁵



In a similar way, a mixture consisting of 2% boron trifluoride etherate in trifluoroacetic acid and triethylsilane brings about the regioselective reduction of the acyclic carbonyl group of the diketovinyl chloride shown in Eq. 215 in high yield (>94%), but with formation of approximately equal amounts of the two possible diastereomers formed from the creation of a new chiral center.³⁹⁶

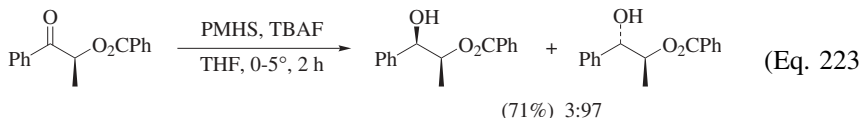
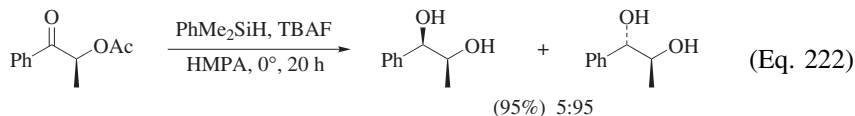
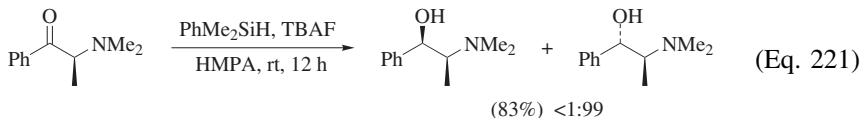
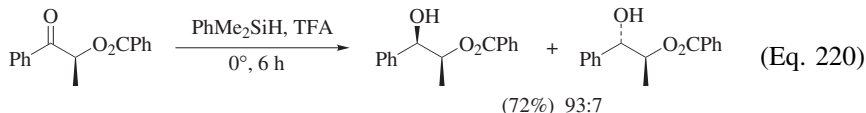
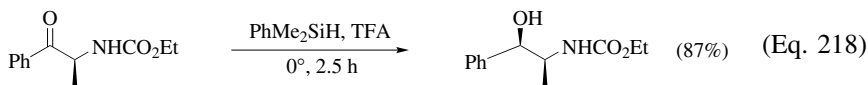


The stereoselective reduction of the carbonyl group of β -hydroxy ketones can be accomplished by a silylation-intramolecular reduction sequence. The best results are obtained when diisopropylchlorosilane is employed.³⁹⁷ The clever use of an intramolecular hydride transfer from a pre-anchored silyl hydride site allows β -hydroxy ketones to be reduced to 1,3-diols with a very high degree of diastereoselectivity.^{397–399} A specific example is the reaction of the hydroxy ketone shown in Eq. 216, first with chlorodiisopropylsilane to form the acyclic siloxane and then with a Lewis acid catalyst to cause intramolecular hydride transfer with formation of a pair of cyclic trans- and cis-disiloxanes. The respective anti- and syn-diols are obtained after fluoride ion catalyzed hydrolysis. The trans:cis ratio of the disiloxane intermediates varies with the Lewis acid employed: TiCl_4 (30 : 1), $\text{MgBr}_2 \cdot \text{OEt}_2$ (60 : 1), SnCl_4 (120 : 1), and $\text{BF}_3 \cdot \text{OEt}_2$ (320 : 1).^{397–399} A similar reduction with chlorodimethylsilane also gives good results (Eq. 217).⁴⁰⁰

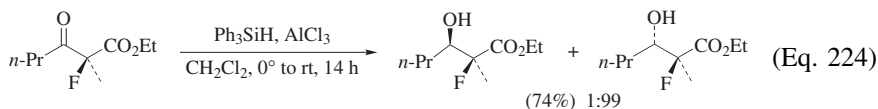


The diastereoselectivity of the reduction of α -substituted ketones has been the subject of much investigation. The reagent combination of trifluoroacetic acid and dimethylphenylsilane is an effective method for the synthesis of erythro isomers of 2-amino alcohols, 1,2-diols, and 3-hydroxyalkanoic acid derivatives.^{86,87,276,375} Quite often the selectivity for formation of the erythro isomer over the threo isomer of a given pair is $>99:1$. Examples where high erythro preference is found in the products are shown below (Eqs. 218–220).²⁷⁶ Similar but complementary results are obtained with $\text{R}_3\text{SiH/TBAF}$, where the threo isomer product

predominates (Eqs. 221 and 222).^{86,87,320} The threo isomer also predominates with the PMHS/TBAF system (Eq. 223).⁴⁰¹

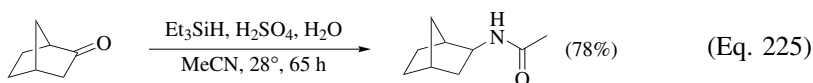


α -Fluoroketo esters are reduced with high stereoselectivity but in only moderate yields with the combination Ph_3SiH (or PhMe_2SiH)/ AlCl_3 (Eq. 224).⁹⁰ The use of PhMe_2SiH /TBAF does not give comparable selectivities.⁹⁰

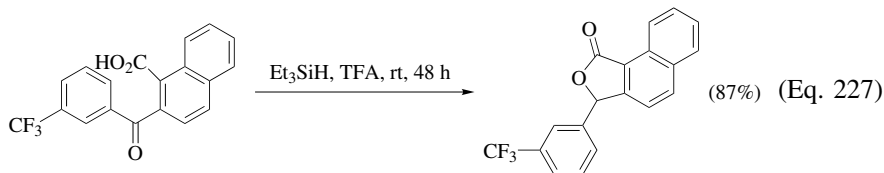
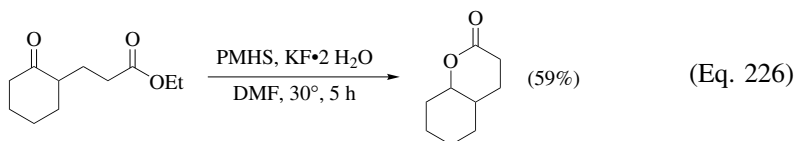


Other systems that are highly stereoselective in the reduction of 2-substituted ketones include PMHS /Triton[®]-B (erythro:threo = 95 : 5),²⁷⁸ $(\text{TMSO})_3\text{SiH}$ /Triton[®]-B (erythro:threo = 95 : 5),²⁷⁸ and PhMe_2SiH /TASF/HMPA (erythro:threo = 93 : 7).³²⁰

Reductive Amidation. The Et_3SiH reduction of ketones in the presence of acid and acetonitrile results in the reductive amidation of the ketone (Eq. 225).³¹³ Ethers and carbinols may be by-products.

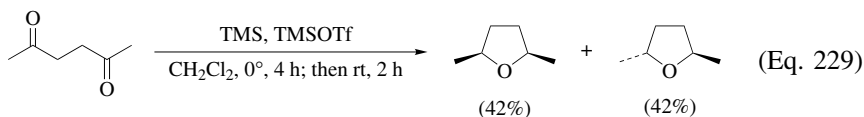
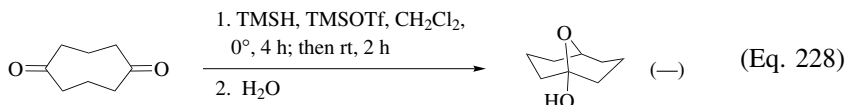


Reductive Esterification. Organosilane reductions of γ - or δ -keto acids and esters provide the corresponding lactones as the final products (Eqs. 226 and 227).^{69,79,402}



Reductive Etherification. The organosilane reduction of ketones can result in the direct formation of symmetrical ethers. The treatment of ketones with $\text{Et}_3\text{SiH}/\text{BiBr}_3$ (or BiCl_3) gives good yields of the symmetrical ethers. The reaction is much better with aldehydes than with ketones, with acetophenone and benzophenone giving only traces of the ether.^{332,343} Benzophenone is converted into bis(diphenylmethyl)ether in good yield with $(\text{HMe}_2\text{Si})_2\text{O}/\text{TMSOTf}$.³¹⁴ The treatment of various ketones with $\text{Et}_3\text{SiH}/\text{TMSOTf}$ (or TMSI) leads to the symmetrical ethers in excellent yields.³³⁴ Treatment of cyclohexanone with $(n\text{-Bu})_3\text{SiH}/\text{TFA}$ gives dicyclohexyl ether and cyclohexyl trifluoroacetate with formation of the ether favored at lower temperatures.³¹³ Other combinations of triethylsilane and various catalysts all result in the formation of mixtures of the ether and the silyl ether of the corresponding alcohol.^{70,313,353} The PEHS/TFA combination also converts cyclohexanone into a mixture of the ether and the trifluoroacetate.²⁰⁷

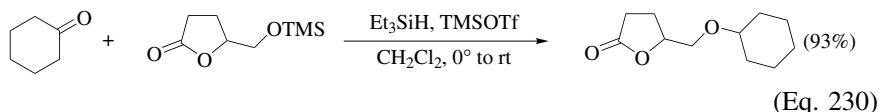
It is possible to form cyclic ethers from diketones as seen by the cyclic hemiketal formed by the reduction of 1,5-cyclooctanedione (Eq. 228) and the conversion of 2,5-hexanedione into *cis*- and *trans*-2,5-dimethyltetrahydrofuran (Eq. 229).³⁹² A naphthopyran can be formed in a similar manner.³³⁹



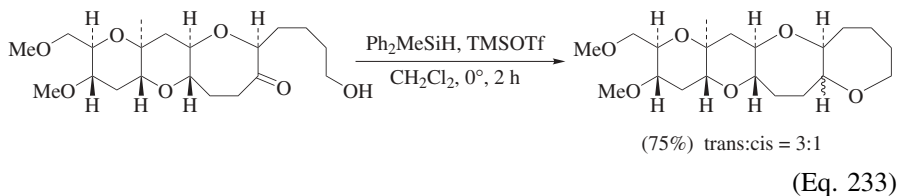
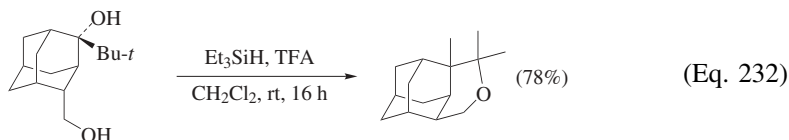
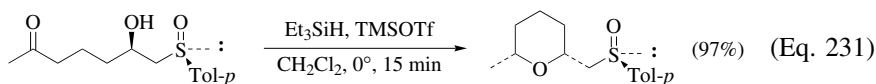
The organosilane reduction of ketones in the presence of alcohols provides an excellent route to unsymmetrical ethers. The reaction of cyclohexanone with ethanol and $\text{Et}_3\text{SiH}/\text{TFA}$ gives cyclohexyl ethyl ether in good yield.^{327,328} The

same conversion can be accomplished with $\text{Et}_3\text{SiH}/\text{HC}(\text{OEt})_3/\text{HCl}$.³²⁷ Adamantanone provides adamantyl methyl ether when treated with $\text{Et}_3\text{SiH}/\text{HC}(\text{OMe})_3/\text{Nafion}^\text{®}\text{-H}$,³³⁵ and adamantyl cyclohexyl ether with $\text{Et}_3\text{SiH}/\text{TMSI}/c\text{-C}_6\text{H}_{11}\text{OTMS}$, but diadamantyl ether with $\text{Et}_3\text{SiH}/\text{TMSOTf}$.³³⁴

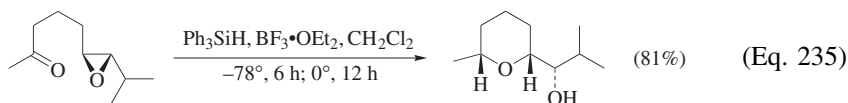
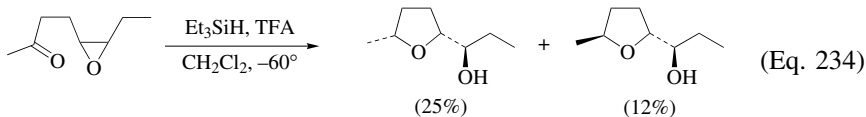
The employment of the trimethylsilyl ether of an alcohol as the partner to ketones in the synthesis of unsymmetrical ethers is highly useful. Ketones react with trimethylsilyl ethers in an electrolytic process with Et_3SiH or PhMe_2SiH as the reducing agent.³³³ Benzyloxytrimethylsilane with $\text{Et}_3\text{SiH}/\text{BiBr}_3$ provides unsymmetrical benzyl ethers in high yields from ketones and aldehydes with aldehydes being more reactive.³⁴³ The reaction has been carried out with both the trimethylsilyl ethers of secondary alcohols and hindered ketones.³³⁴ The combination of $\text{Et}_3\text{SiH}/\text{TMSOTf}/\text{ROTMS}$ gives good yields of the desired ethers (Eq. 230).³⁴¹



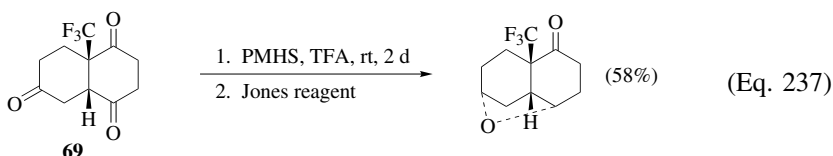
The cyclization of γ -hydroxy ketones is useful for the formation of pyrans,^{306,403} both directly and via rearrangement, as illustrated in Eq. 231.¹⁵³ As with their acyclic counterparts, these cyclizations also occur with the silyl ethers of the hydroxy ketones where $\text{Et}_3\text{SiH}/\text{BiBr}_3$ is used with the TBS and TES ethers.^{342,404} A methyl thiomethyl ether is also capable of undergoing the reductive cyclization.⁴⁰⁵ In like manner, 1,4-diols and ε -hydroxy ketones provide oxepanes, with Et_3SiH or $\text{PhMe}_2\text{SiH}/\text{TMSOTf}$ being especially effective (Eqs. 232 and 233).^{336,406} The trimethylsilyl ether of the alcohol also provides the oxepane.³⁰⁶



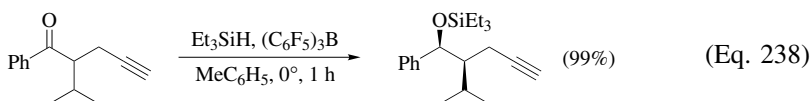
The reductive ether formation from keto epoxides is an acid-catalyzed process (Eqs. 234⁴⁰⁷ and 235⁴⁰⁸).



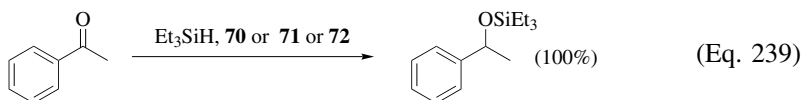
Diketones are reductively cyclized in a TFA-catalyzed reaction. The cyclization of the cage structure shown in Eq. 236 illustrates this ring closure in the formation of an acetal of trifluoroacetaldehyde.⁴⁰⁹ The organosilane reduction of triketone **69** followed by Jones oxidation gives the cyclic ketoether in fair yield (Eq. 237).⁴¹⁰

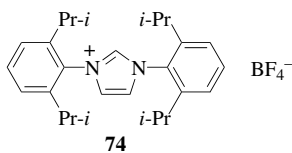
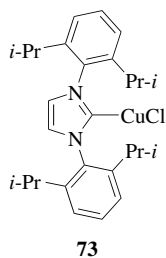
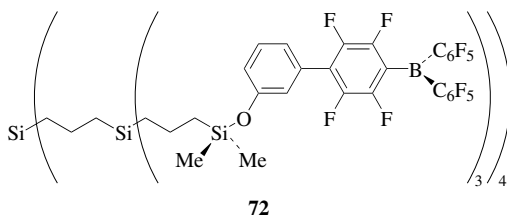
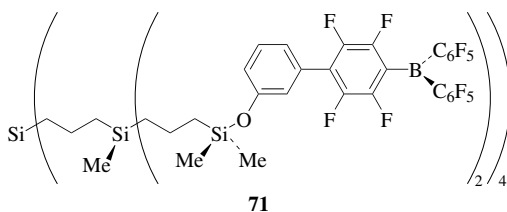
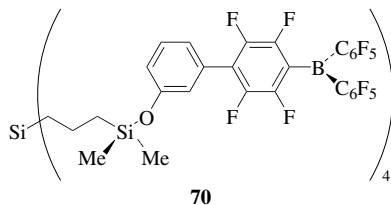


Reductive Silylation. The reductive silylation of ketones and subsequent deprotection of the silylated alcohol to the alcohol can be accomplished in a variety of ways. Phenyldimethylsilane in the presence of KF, CsF, or RbF gives the (1-phenylethoxy)phenyldimethylsilane from acetophenone in high yields.^{345–347} The reagent combination of $\text{Ph}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$ gives good yields of the silyl ether with aryl ketones.¹¹⁵ The combination of $\text{Et}_3\text{SiH}/(\text{C}_6\text{F}_5)_3\text{B}$ gives an excellent yield of silyl ether with threo selectivity in the reduction of α -substituted ketones (Eq. 238).³⁷²

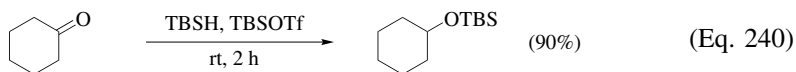


The reduction of ketones or aldehydes with $\text{Ph}_2\text{SiH}_2/\text{KF}$ produces either the mono- or dialkoxydiphenylsilane depending on the stoichiometry of the reaction.^{75,319} The dendrimeric catalysts **70**, **71**, or **72** work with Et_3SiH to give the silyl ether of acetophenone in excellent yield (Eq. 239).¹¹⁷

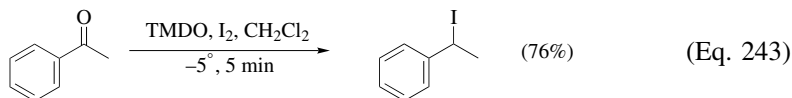
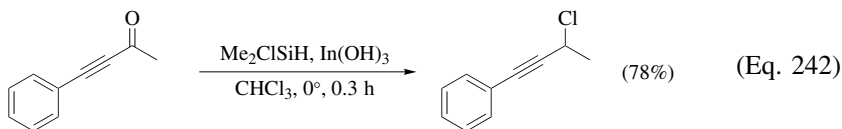
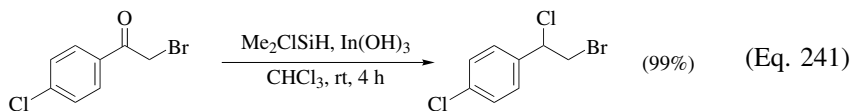




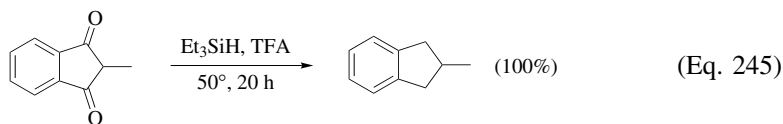
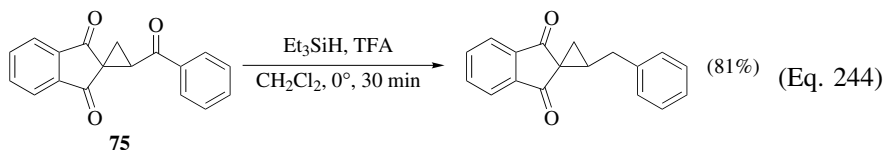
Benzil is reductively triethylsilylated to the bis(silyl) ether in 83% yield.⁴¹¹ The combination of $\text{Et}_3\text{SiH}/\text{ZnCl}_2$ reductively triethylsilylates ketones in good yield.³⁸² Excellent yields of triethylsilyl ethers from ketones are accomplished with the use of triethylsilane and catalyst **73** or **74**.⁴¹² *tert*-Butyldimethylsilyl ethers can be synthesized by the reaction of TBSH/TBSOTf with a ketone (Eq. 240).³⁹²



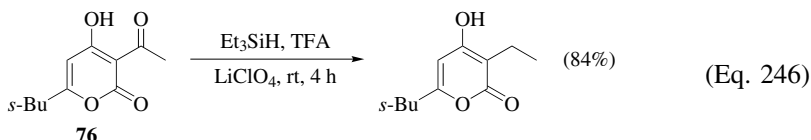
Reduction to Halocarbons. The best conditions for the reductive chlorination of ketones use the reagent combination $\text{Me}_2\text{ClSiH}/\text{In}(\text{OH})_3$ (Eq. 241).³³¹ Examples include conversions of aryl ketones to benzyl chlorides, ethynyl ketones to propargyl chlorides, and alkyl ketones to alkyl chlorides (Eq. 242).³³¹ Addition of lithium iodide to the reaction mixture yields the corresponding iodide product. The combination of TMDO/ I_2 reductively iodinates aryl ketones and aldehydes in good yields (Eq. 243).³⁵⁷



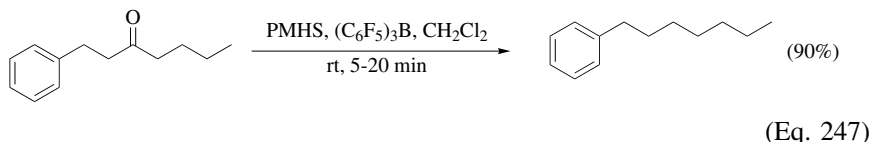
Reduction to Alkanes. Carbonyl groups can be reductively deoxygenated to methylene functions if both of the two steps represented by Eqs. 1 and 2 are followed to completion. The direct reduction of a carbonyl function to a methylene group is an important reaction of organosilanes that is applicable to a variety of ketones. A number of reagents have been employed in the direct reduction of aromatic ketones such as acetophenone to the corresponding methylene derivatives. These include $\text{Et}_3\text{SiH}/\text{BF}_3 \cdot \text{OEt}_2$,^{210,217,375,413} $\text{Et}_3\text{SiH}/\text{TFA}$,^{73,135,180,207,210,257,376,414-419} $\text{Et}_3\text{SiH}/\text{HCO}_2\text{H}$,²⁰⁸ $\text{Et}_3\text{SiH}/\text{HClO}_4$,²¹⁴ $\text{Et}_3\text{SiH}/\text{AlCl}_3/\text{HCl}$,¹³⁶ $\text{Et}_3\text{SiH}/\text{CF}_3\text{SO}_3\text{H}$,⁴²⁰ $\text{ClMe}_2\text{SiH}/\text{In}(\text{OH})_3$,³³¹ $\text{PMHS}/(\text{C}_6\text{F}_5)_3\text{B}$,³⁵⁴ $\text{Et}_3\text{SiH}/\text{TFA}/\text{NH}_4\text{F}$,¹³⁵ and Et_3SiH (or $\text{PhMe}_2\text{SiH}/\text{TiCl}_4$).⁴²¹ Diaryl ketones are reduced with $\text{Et}_3\text{SiH}/\text{PPHF}$ (pyridinium poly(hydrogen fluoride)) in excellent yields.¹³⁵ The triketone **75** is reduced to a diketone in good yield using $\text{Et}_3\text{SiH}/\text{TFA}$ at 0° (Eq. 244).⁴¹⁸ On the other hand, 2-methyl-2*H*-indene-1,3-dione is reduced completely to 2-methyl-2,3-dihydro-1*H*-indene at elevated temperature (Eq. 245).⁴²²



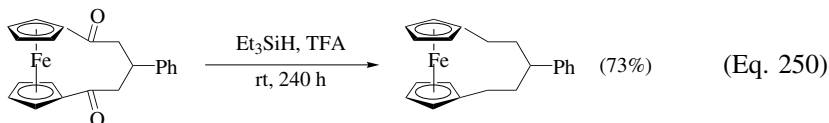
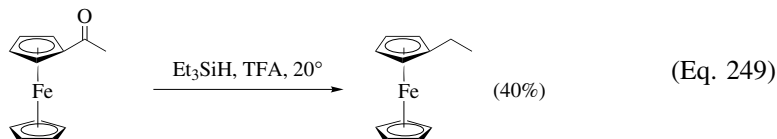
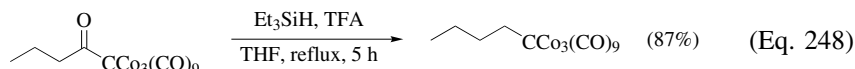
The reduction of 2-acetylfuran to 2-ethylfuran is possible with $\text{Et}_3\text{SiH/TFA/BF}_3\cdot\text{OEt}_2$ (80%).²¹¹ Both $\text{Et}_3\text{SiH/AlCl}_3$ ²⁵⁹ and $\text{Et}_3\text{SiH/TFA}$ ²⁵⁷ reduce 2-acetylthiophene to 2-ethylthiophene without any reduction of the thiophene group. A series of strong acid catalysts and various silanes was used to study the reduction of ketones, with aliphatic ketones leading to the corresponding ethers and aromatic ketones providing methylene compounds.³⁵³ The acylpyrone **76** is also reduced to the methylene derivative in good yield (Eq. 246).⁴²³



The triflic acid catalyzed triethylsilane reduction of cyclohexanone gives cyclohexane, albeit in low yield.⁴²⁰ 2-Methylcyclohexanone is reduced to methylcyclohexane and adamantanone to adamantane with $\text{EtMe}_2\text{SiH/BF}_3$ in good yield.¹ Adamantanone is also reduced to adamantane with $\text{Et}_3\text{SiH/BF}_3\cdot\text{OEt}_2$ ²¹⁷ and TMSH/NaTFPB.⁴²⁴ The reagent PMHS/ $(\text{C}_6\text{F}_5)_3\text{B}$ effects the reduction of alkyl ketones to methylenes.³⁵⁴ Thus, 1-phenyl-3-heptanone is reduced to 1-phenylheptane in excellent yield under these conditions (Eq. 247).

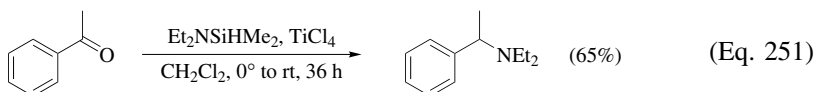


Acyl cobalt complexes are reduced to their alkyl counterparts in good yields with $\text{Et}_3\text{SiH/TFA}$ (Eq. 248).^{183,310,425} Acyl ferrocene derivatives are reduced to the respective methylene compounds with $\text{Et}_3\text{SiH/TFA}$ (Eqs. 249¹⁸⁰ and 250).¹⁷⁹ Acylcyclopentadienylmanganese tricarbonyl is similarly reduced in good yield.³⁵¹

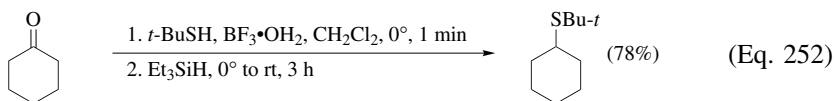


Reductive Amination. An excellent application of organosilane reductions is found in the reductive amination of ketones. This method is a useful alternative

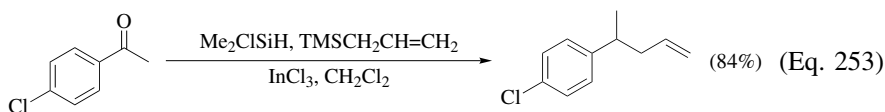
to the cyanoborohydride approach to this transformation. In one version the ketone is reacted with *N,N*-diethylaminodimethylsilane, thus incorporating both the amine and the hydride in a single organosilane reagent (Eq. 251).³⁵⁹ Other aminosilanes are also useful in this sequence. Another version of this transformation makes use of the inexpensive PMHS reducing agent to react a ketone directly with an amine in a two-step, one-pot, high-yield reaction.³⁶³ The $\text{PhSiH}_3/(n\text{-Bu})_2\text{SnCl}_2$ combination also reductively aminates ketones in good yields.³⁶¹



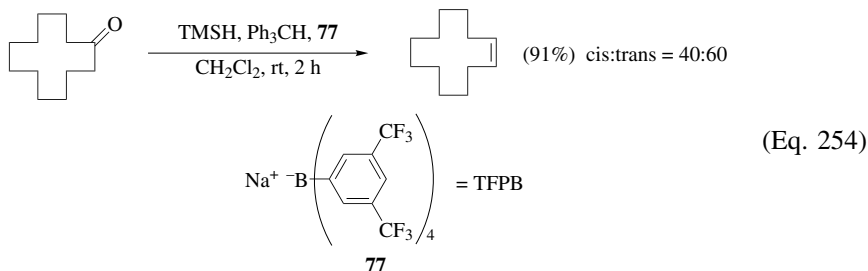
Reductive Thiolation. Ketones are reductively thiolated when treated first with a thiol under acidic conditions followed by addition of a silane (Eq. 252).^{365,426}



Miscellaneous Ketone Reductions. The reductive allylation of aromatic ketones occurs with the reagent combination of Me_2ClSiH /allyltrimethylsilane/ InCl_3 (Eq. 253).⁴²⁷

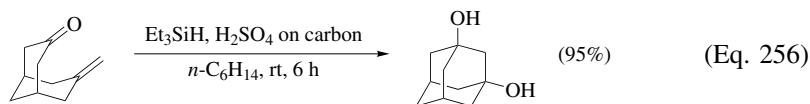
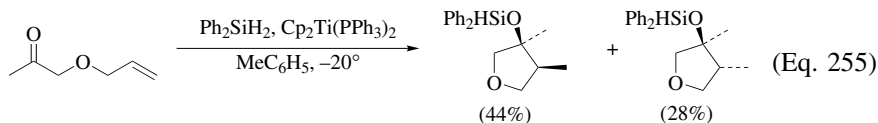


Cyclododecanone is reduced to a mixture of *cis*- and *trans*-cyclododecene in high yield with trimethylsilane and tetrakis-3,5-bis(trifluoromethylphenyl)borate (TFPB, **77**) (Eq. 254).⁴²⁴



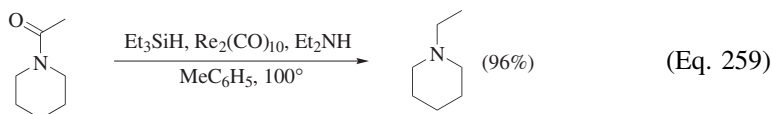
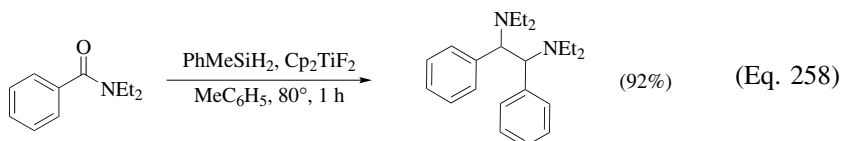
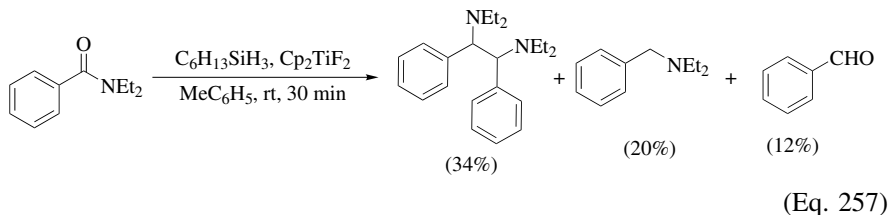
Because the organosilane reduction of ketones passes through a positively charged intermediate via the complexation or protonation of the carbonyl oxygen, the presence of suitably placed $\text{C}=\text{C}$ functions can lead to cyclizations with the hydride of the silane adding to the $\text{C}=\text{C}$ group. This strategy applies to

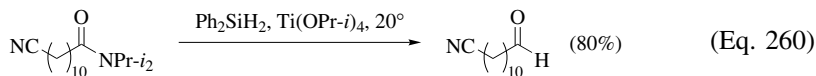
a number of conversions of δ,ϵ -unsaturated ketones into tetrahydrofuran derivatives (Eq. 255).^{428,429} In these systems, the cyclization is clearly favored over the simple carbonyl reduction pathway. The phenylsilane reduction of 6-methylhept-5-ene-2-one results in the straightforward 1,2-reduction of the carbonyl group to the alcohol.^{79,320,358} Under different conditions involving sulfuric acid, cyclization and hydration is preferred over reduction (Eq. 256).²⁴³



Reduction of Amides

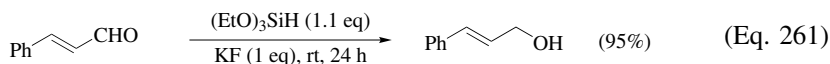
The organosilane/ Cp_2TiF_2 reduction of *N,N*-diethylbenzamide illustrates the various possible pathways of reductive coupling, carbonyl reduction, and aldehyde formation (Eq. 257).⁴³⁰ Conditions have been developed for all of these pathways. The combination of $\text{PhMeSiH}_2/\text{Cp}_2\text{TiF}_2$ gives good to excellent yields of the 1,2-diamine in nearly equal molar ratios of meso to racemic diastereomers (Eq. 258).⁴³⁰ On the other hand, conditions for the reduction of amides to the amines include the use of $\text{Ph}_2\text{SiH}_2/\text{HRh}(\text{CO})(\text{PPh}_3)_3$,⁴³¹ various silanes with ruthenium catalysts,⁴³² the $\text{EtMe}_2\text{SiH}/\text{Ru}$ -complex,²⁸⁰ and $\text{Et}_3\text{SiH}/$ various Mn, Ru, Re, Os, Rh, Ir, Pd, and Pt catalysts.⁴³² All of these reducing systems give high yields of the amine (Eq. 259). The reduction of an amide to the aldehyde is best accomplished with $\text{Ph}_2\text{SiH}_2/\text{Ti}(\text{OPr-}i)_4$ wherein the yields range from 65% to 90% (Eq. 260).⁴³³



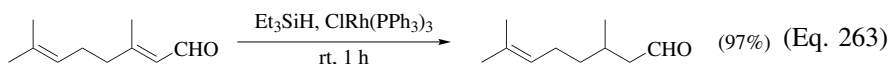
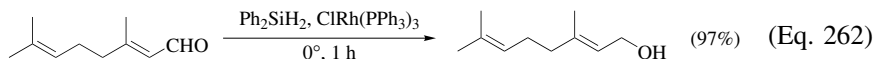


Reduction of α,β -Unsaturated Aldehydes

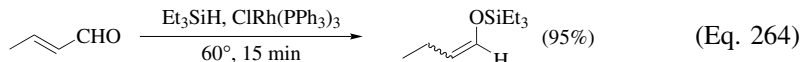
When carried out under standard conditions with $\text{Et}_3\text{SiH/TFA}$, reduction of acrolein leads to a mixture of allyl alcohol, 1-propanol, and di-*n*-propyl ether in addition to allyl trifluoroacetate and *n*-propyl trifluoroacetate.⁴³⁴ The 1,2-reduction of cinnamaldehyde with triethoxysilane in the presence of fluoride ion provides the corresponding allyl alcohol in good yields (Eq. 261).



Diphenylsilane catalyzed by various salts promotes the 1,2-reduction of cinnamaldehyde.³¹⁸ Cesium fluoride catalysis is particularly effective.³²⁰ It is possible to stop these reactions at the silyl ether stage.^{73,320} The 1,2-reduction of citral is accomplished in high yield with diphenylsilane and Wilkinson's catalyst (Eq. 262).⁴³⁵ Interestingly, the trialkylsilanes, ethyldimethylsilane and triethylsilane, give high yields of the 1,4-reduction product whereas diisopropylsilane gives a 1 : 1 mixture of 1,2- and 1,4-reduction (Eq. 263).⁴³⁵



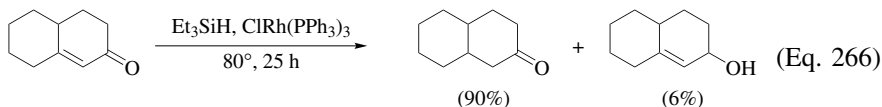
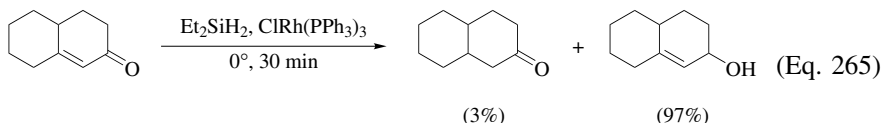
The 1,4-reduction of α,β -unsaturated aldehydes is best carried out with diphenylsilane in the presence of zinc chloride and tetrakis(triphenylphosphine) palladium⁴³⁶ or a combination of triethylsilane and tris(triphenylphosphine) chlororhodium.⁴³⁷ Other practical approaches use phenylsilane with nickel (0) and triphenylphosphine⁴³⁸ and diphenylsilane with cesium fluoride.⁸³ It is possible to isolate the initial silyl enol ether intermediate from the 1,4-hydrosilylation of α,β -unsaturated aldehydes (Eq. 264).^{73,411} The silyl enol ethers are produced as a mixture of *E* and *Z* isomers.



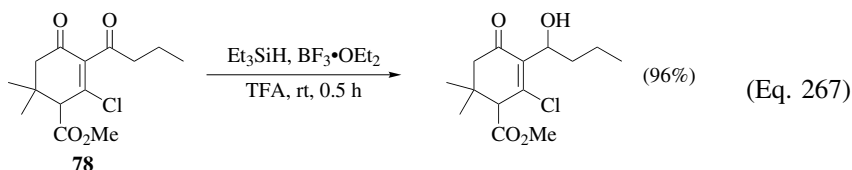
Reduction of α,β -Unsaturated Ketones

The 1,2-hydrosilylation of α,β -unsaturated ketones is possible and provides a convenient route to allyl alcohols. The standard conditions of $\text{Et}_3\text{SiH/TFA}$ lead to overreduction to the saturated alcohol with mesityl oxide.^{434,439} The combination of $\text{Et}_3\text{SiH/AlCl}_3/\text{HCl}$ with mesityl oxide gives a mixture of the 1,2-reduction product 4-methylbut-3-ene-2-ol and the fully reduced product, 2-methylpent-2-ene.¹³⁶ The $\text{Ph}_2\text{SiH}_2/\text{RhH}(\text{PPh}_3)_4$ reduction of cyclohexenone gives reaction at

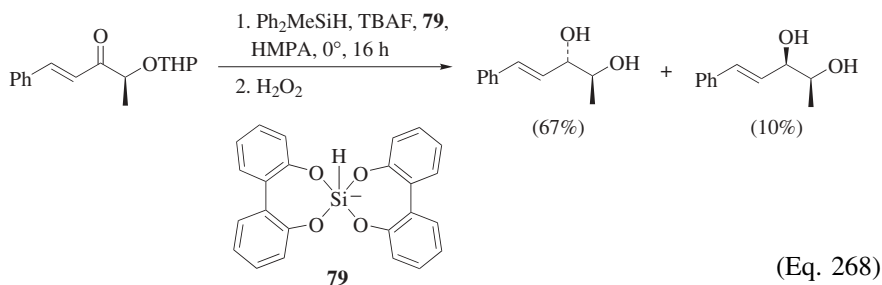
both the C=O and the C=C bonds, resulting in a mixture of cyclohexenol and cyclohexanol, with cyclohexenol predominating.³²⁰ Diethylsilane, diphenylsilane, or phenylsilane with Wilkinson's catalyst effectively reduce the carbonyl group of α,β -unsaturated ketones (Eq. 265).⁴³⁵ Under similar conditions, triethylsilane gives predominantly reduction of the C=C bond (Eq. 266).⁴³⁵



The triethylsilane reduction of the alkylidene-1,3-dione **78** occurs in a 1,2-fashion at the acyclic carbonyl group (Eq. 267).³⁹⁶

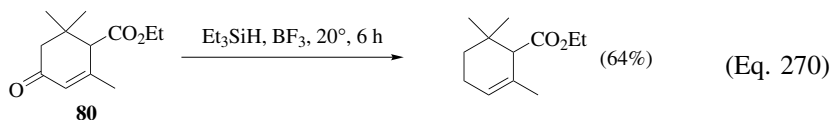
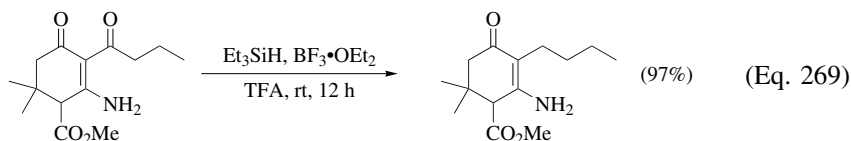


The 1,2-reduction of enones is also accomplished with the combination of $\text{PhMe}_2\text{SiH/TBAF}$, conditions that show good anti stereoselectivity in the reduction of α' -substituted- α,β -unsaturated ketones (Eq. 268).^{86,440} Similar behavior is seen with the reagent combinations $\text{Ph}_2\text{SiH}_2/\text{CsF}$,³²⁰ $\text{Ph}_2\text{SiH}_2/\text{RhH(PPh}_3)_4$,³⁷⁴ and $(\text{EtO})_3\text{SiH/CsF}$.⁸⁰ Cyclohexenone is reduced to cyclohexenol with hydridosilicates such as **79**.^{90,93} The triethylsilane/TFA reduction of dibenzylidene ketone causes reduction of the carbonyl group along with both double bonds to give 1,5-diphenyl-3-pentanol in 85% yield.^{434,439}

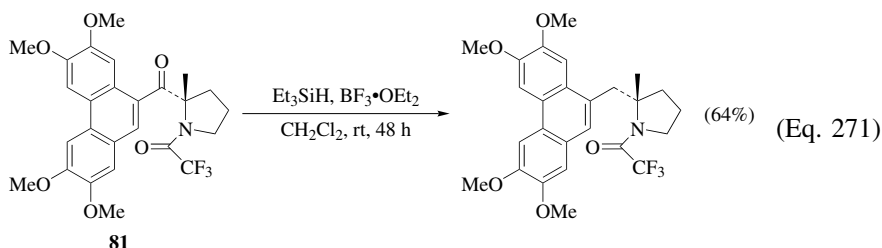


The full reduction of a carbonyl to a methylene group occurs with certain β -aminoalkylidene-1,3-diones (Eq. 269).^{395,441} A similar reduction is seen with

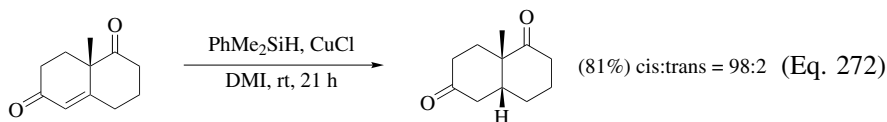
the β -methoxy- and β -chloro analogs.³⁹⁶ The γ -(carboxyethyl)cyclohexenone **80** is fully reduced to the methylene derivative (Eq. 270).^{434,439,442}



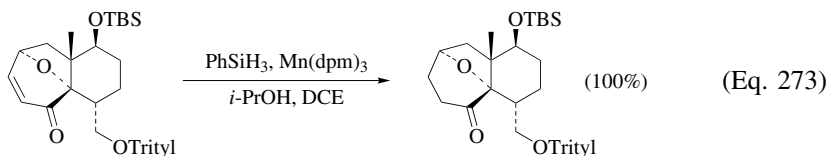
α,β -Unsaturated α -aryl ketones can be reduced to the methylene compounds without concomitant reduction of the C=C bond. Enone **81** is reduced in a 1,2-fashion to the corresponding methylene compound (Eq. 271).⁴⁴³



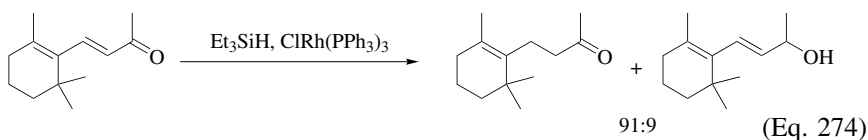
The 1,4-hydrosilylation of enones can be accomplished under a variety of conditions using various reagent combinations. Among the useful ones are: $\text{Et}_3\text{SiH/TFA}$,^{266,434,439} $\text{Ph}_2\text{SiH}_2/\text{RhH}(\text{PPh}_3)_4$,³⁷⁴ $\text{PhMe}_2\text{SiH/CuF}$ (or $\text{CuCl}(\text{PPh}_3)_3$),^{444–446} $\text{PMHS/Pd-nanocomposite}$,²¹⁹ $\text{Ph}_2\text{SiH}_2/\text{ZnCl}_2/\text{Pd}(\text{PPh}_3)_4$,⁴³⁶ $\text{Et}_3\text{SiH/RhCl}(\text{PPh}_3)_3$,⁴³⁵ $\text{Ph}_2\text{SiH}_2/\text{RhCl}(\text{PPh}_3)_3$,⁴³⁵ $\text{PhSiH}_3/\text{RhCl}(\text{PPh}_3)_3$,⁴³⁵ $\text{EtMe}_2\text{SiH/RhCl}(\text{PPh}_3)_3$,⁴³⁵ $\text{PhSiH}_3/[\text{CuH}(\text{PPh}_3)]_6$,⁴⁴⁷ $\text{Ph}_2\text{SiH}_2/\text{CsF}$,⁸³ $\text{PhSiH}_3/\text{Mn}(\text{dpm})_3$,⁴⁴⁸ $\text{Et}_3\text{SiH/TiCl}_4$,^{435,449} $\text{Ph}_3\text{SiH/Mo}(\text{CO})_6$,⁴⁵⁰ $\text{PhMe}_2\text{SiH/CuF}(\text{PPh}_3)_3$,^{444,445} $\text{Cl}_3\text{SiH/Ni/CoCl}_2$,⁴⁵¹ and PMHS/Pd/C .³¹⁶ All of these methods show good to excellent selectivity for 1,4- over 1,2-hydrosilylation. The $\text{PhMe}_2\text{SiH/CuCl}$ system reduces the unsaturated diketone in Eq. 272 with a high degree of cis-selectivity.⁴⁴⁵



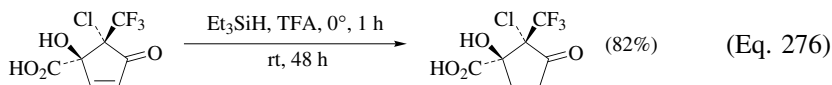
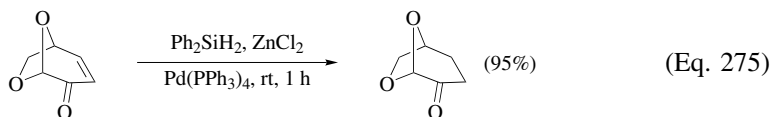
The $\text{PhSiH}_3/\text{Mn}(\text{dpm})_3$ combination nicely reduces the conjugated C=C bond in a polyfunctional ketone without affecting the trityl group or causing reaction at the α -alkoxyketone function (Eq. 273).⁴⁴⁸



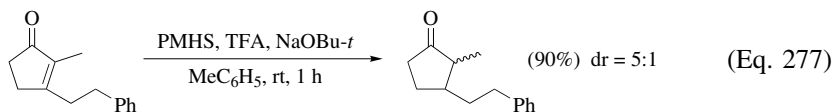
$\alpha,\beta,\gamma,\delta$ -Unsaturated ketones are reduced at the α,β -double bond with the combination $\text{PhMe}_2\text{SiH}/\text{RhCl}(\text{PPh}_3)_3$ (Eq. 274).^{437,452} Employment of diethylsilane or diphenylsilane results in only the 1,2-hydrosilylation products.



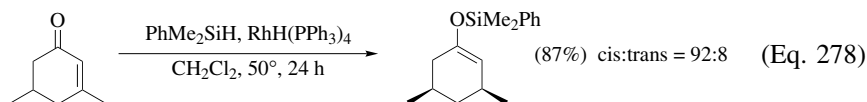
The 1,4-reduction of an enone in the presence of a ketal is shown in Eq. 275.⁴³⁶ The $\text{Et}_3\text{SiH}/\text{TFA}$ system reduces the polyfunctional cyclic α,β -enone in Eq. 276 without affecting the α -hydroxy carboxyl or α -chloro keto groups.⁴⁵³



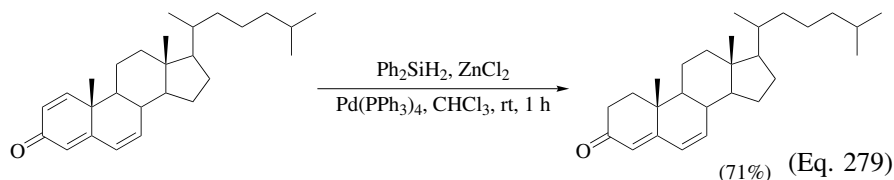
The use of PMHS/TFA and a base leads to the 1,4-reduction of enones (Eq. 277).⁴⁵⁴



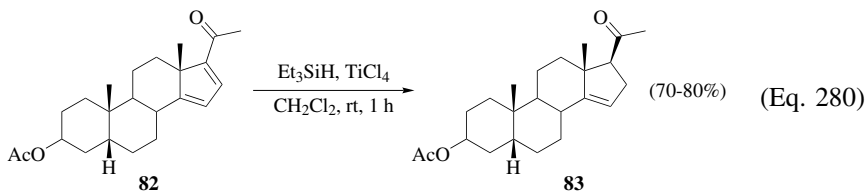
The 1,4-hydrosilylation of enones can be used as a method for the introduction of the silyl enol ether functionality, and may be accomplished with the combination of $\text{PhMe}_2\text{SiH}/\text{RhH}(\text{PPh}_3)_4$ (Eq. 278),³⁷⁴ $\text{Et}_3\text{SiH}/\text{RhCl}(\text{PPh}_3)_3$,⁴¹¹ $(\text{HMe}_2\text{Si})_2\text{O}/[\text{CuH}(\text{PPh}_3)]$,⁴⁵⁵ $\text{Et}_3\text{SiH}/\text{Pt}$ -complex,⁴⁵⁶ chloromethyldimethylchlorosilane/ $\text{RhH}(\text{PPh}_3)_4$,³⁷⁴ or $\text{Ph}_3\text{SiH}/\text{RhCl}(\text{PPh}_3)_3$.⁴¹¹



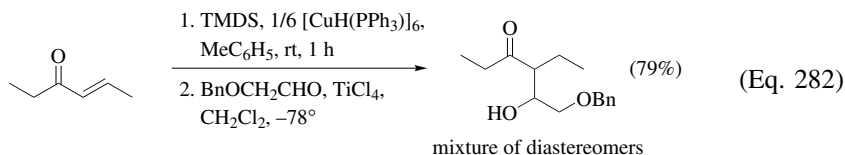
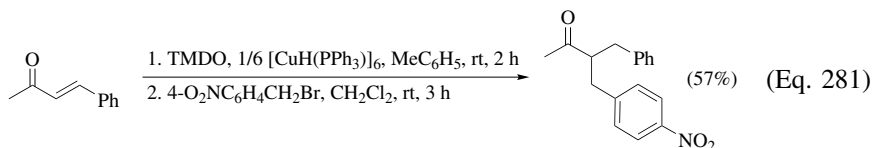
Several steroidal α,β -unsaturated ketones have been subjected to silane reductions. In particular, enones of ring A have been reduced in a 1,4-manner to give the saturated ketone with a preference for trans AB ring fusion. This and comparable transformations are nicely accomplished with the $\text{Ph}_2\text{SiH}_2/\text{ZnCl}_2/\text{Pd}(\text{PPh}_3)_4$ system (Eq. 279)⁴⁵⁷ used in the 1,4-reduction of non-steroidal enones. Other conditions for this transformation use $\text{Et}_3\text{SiH}/\text{TiCl}_4$ ⁴⁴⁹ and $\text{Et}_3\text{SiH}/\text{TFA}$,²⁴³ but these lead to mixed stereochemistry at the AB ring fusion. The $\text{PhSiH}_3/\text{Mo}(\text{dpm})_3$ combination is also used for this reduction.⁴⁴⁸

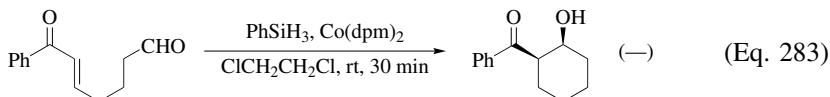


The conjugated dienone **82** reacts with $\text{Et}_3\text{SiH}/\text{TiCl}_4$ to yield the nonconjugated product **83** shown in Eq. 280.⁴⁴⁹ Other analogous dienones behave similarly with triethylsilane, but TMDO gives the best yields.⁴⁵⁸

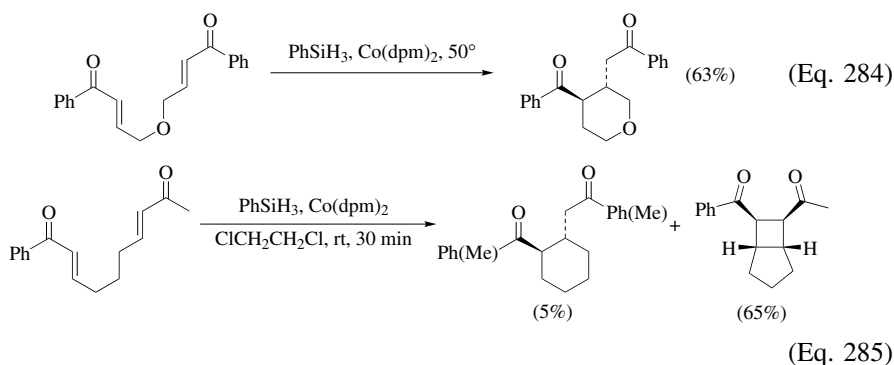


The intermediate enolate or enol ether from the initial reduction of an enone may be alkylated in situ (Eq. 281).⁴⁵⁵ β -Substituted cyclopentenones may be asymmetrically reduced and alkylated⁴⁵⁹ (see section on asymmetric reductions of enones). Enolates may also be trapped with an aldehyde in a reductive aldol condensation of an enone with an aldehyde,⁴⁵⁵ permitting a regioselective aldol condensation to be carried out as shown in Eq. 282.⁴⁵⁵ This class of reductive aldol condensation reactions can also occur in a cyclic manner (Eq. 283).⁴⁶⁰

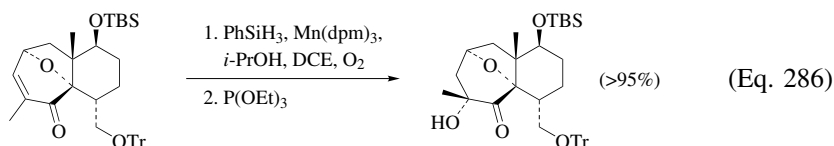




A tandem 1,4-hydrosilylation/Michael addition of suitably arranged bis enones is reported employing the systems $\text{PhSiH}_3/\text{Co}(\text{dpm})_2$ (Eq. 284),^{460,461} various silanes/ $\text{Co}(\text{dpm})_2$,⁴⁶² $\text{PhMe}_2\text{SiH}/\text{Co}(\text{dpm})_2$,⁴⁶⁰ $\text{Et}_3\text{SiH}/\text{AlCl}_3$,⁴⁶¹ and $\text{Et}_2\text{MeSiH}/\text{Rh}_4(\text{CO})_{12}$.⁴⁶⁴ The competing 2 + 2 cycloaddition reaction can be a complication (Eq. 285).⁴⁶⁰

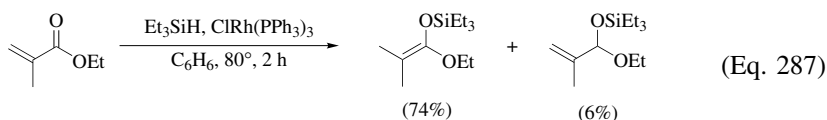


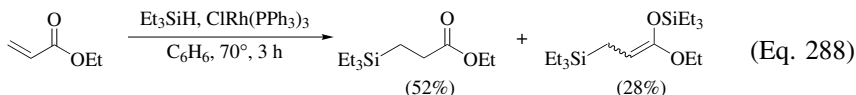
A further example of the trapping of the in situ generated silyl enol ether from the reduction of an enone is the conversion of an enone into an α -hydroxy ketone via oxidation of the silyl enol ether (Eq. 286).⁴⁶⁵



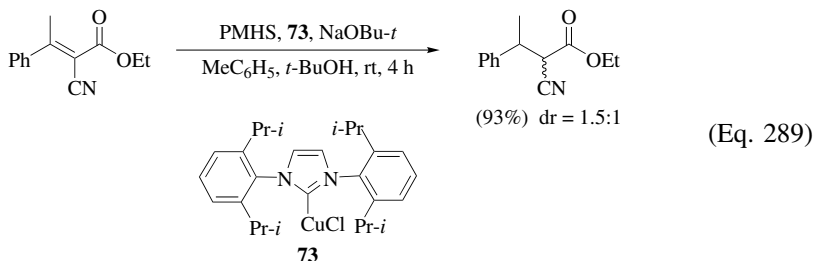
Reduction of α,β -Unsaturated Esters

The reduction of the $\text{C}=\text{C}$ bond of α,β -unsaturated esters has been carried out with various silane/catalyst combinations. The combination of $\text{Et}_3\text{SiH}/\text{RhCl}(\text{PPh}_3)_3$ gives the silyl ketene acetal along with the silylated hemiacetal, the result of the 1,2-reduction of the carbonyl group (Eq. 287).⁴⁶⁶ The use of other silanes in this transformation gives similar results. Acrylates give hydrosilylation of the $\text{C}=\text{C}$ bond, leading to β -silyl esters and their silyl ketene acetals as the major products (Eq. 288).^{466,467}

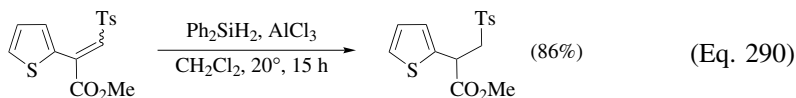




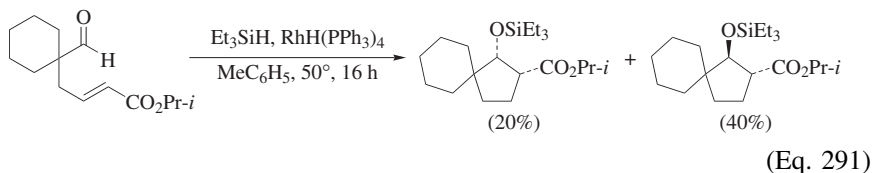
Triethoxysilane and $\text{RhH}(\text{PPh}_3)_4$ produce the silyl ketene acetal in high yield.³⁷⁴ Methyl acrylate is reduced to methyl propionate with $\text{Cl}_3\text{SiH}/\text{CoCl}_2$ ⁴⁴⁸ or PMHS/Pd-nanocomposite catalyst,²¹⁹ and to a mixture of methyl propionate, the methyl β -silylpropionate, and the methyl α -silylpropionate with $\text{R}_3\text{SiH}/\text{H}_2\text{PtCl}_6$ or $\text{R}_3\text{SiH}/\text{RhCl}(\text{PPh}_3)_3$ where $\text{R} = \text{Me}, \text{Et},$ or $n\text{-Pr}$.⁴⁶⁷ The reduction of ethyl acrylate shows similar behavior.^{451,466} The combination of $\text{Et}_3\text{SiH}/\text{Mo}(\text{CO})_6$ works well for the conjugate reduction of α,β -unsaturated esters.⁴⁵⁰ This method appears to be free of some of the side reactions mentioned above. The use of metallic nickel, triphenylphosphine, and phenylsilane reduces α,β -unsaturated esters to the saturated esters in moderate yields.⁴³⁸ Dimethylphenylsilane carries out the same transformation in the presence of CuCl .^{444,445} Triethylsilane and trifluoroacetic acid can reduce α,β -unsaturated esters in good yields⁴⁶⁸ as can $\text{Et}_3\text{SiH}/\text{TMSOTf}$.⁴⁶⁹ Excellent yields of the silane reduction of α,β -unsaturated esters are obtained by the reaction of PMHS and sodium *tert*-butoxide in the presence of catalyst **73** (Eq. 289).⁴⁵⁴



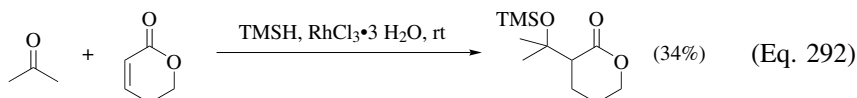
The $\text{Ph}_2\text{SiH}_2/\text{AlCl}_3$ reduction of β -sulfonyl- α,β -unsaturated esters results in the formation of the β -sulfonyl ester. Good yields are obtained and AlCl_3 is the best Lewis acid catalyst for this reaction (Eq. 290).³⁷³



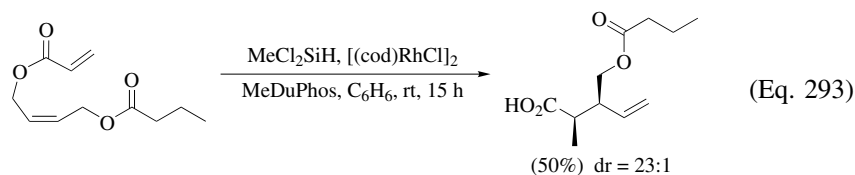
In the reductive aldol condensation of an α,β -unsaturated ester and an aldehyde shown in Eq. 291, the initial step is believed to be the addition of an in situ formed rhodium hydride to the α,β -unsaturated ester, followed by reaction of the resulting rhodium enolate with the aldehyde.⁴⁷⁰ The reaction has been carried out both inter-⁴⁷⁰ and intramolecularly^{471,472} as well as in an asymmetric fashion (Eq. 291).



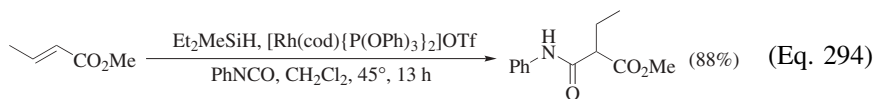
Similarly, methyl methacrylate reacts with ketones and TMSH/RuCl₃·3H₂O to give β -trimethylsiloxy-2,2-dimethyl methyl esters in good yields. A lactone example is shown in Eq. 292.⁴⁷³ Methyl acrylate, trans methyl (*E*)-cinnamate, and 3,4-dehydro- δ -lactone react in an analogous manner, albeit in lower yields.⁴⁷³



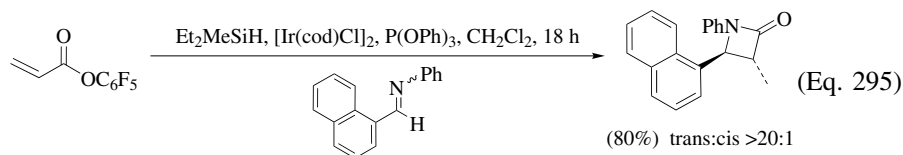
Allyl acrylates have been reacted with the combination of ClMe₂SiH/[codRhCl]₂/Me-DuPHOS (1,2-bis(2,5-dimethylphospholano)benzene) to bring about reduction of the α,β -unsaturated ester followed by a Claisen rearrangement to the γ,δ -unsaturated carboxylic acid (Eq. 293).⁴⁷⁴ Other silanes did not perform as well in this sequence.

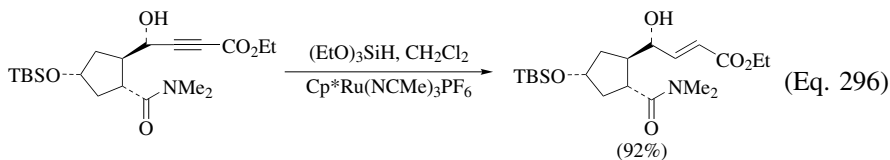


In yet another example of an in situ reductive generation of an enolate, β -amido esters are formed via the reaction of an α,β -unsaturated ester with a silane in the presence of an isocyanate (Eq. 294).⁴⁷⁵ The yields obtained using methyl acrylate and methyl crotonate as substrates are generally excellent.



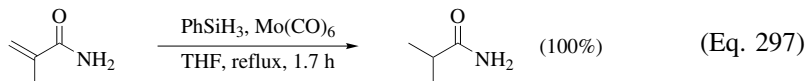
The organosilane reduction of pentafluorophenyl acrylate in the presence of an imine was shown to lead to β -lactams in good yields (Eq. 295).⁴⁷⁶ The conversion of an ethyl ynoate into an *E*-ethyl enoate in high yield is shown in Eq. 296.⁴⁷⁷





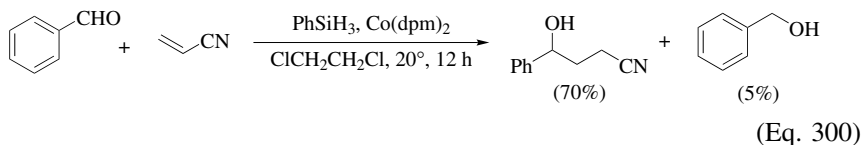
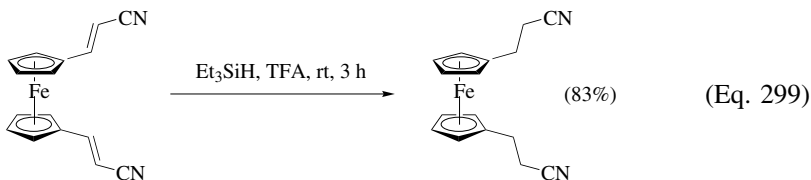
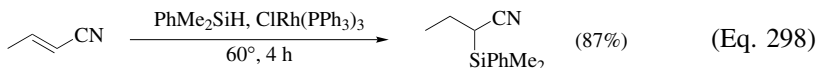
Reduction of α,β -Unsaturated Amides

The conjugate hydrosilylation of α,β -unsaturated amides can be carried out in high yields with $\text{PhSiH}_3/\text{Mo}(\text{CO})_6$ (Eq. 297)⁴⁵⁰ or $\text{Ph}_2\text{SiH}_2/\text{ZnCl}_2/\text{Pd}(\text{PPh}_3)_4$.⁴³⁶ Primary, secondary, and tertiary amides are equally reactive.⁴⁵⁰ The reduction of a β -tributylstannyl- α,β -unsaturated tosylamide is also reported.⁴⁶⁹



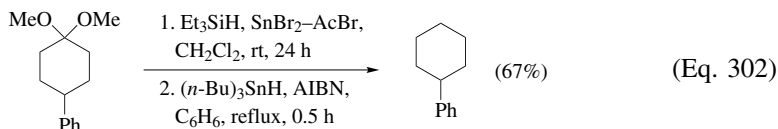
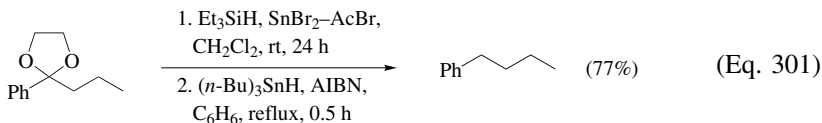
Reduction of α,β -Unsaturated Nitriles

The reaction of α,β -unsaturated nitriles with organosilanes in the presence of Wilkinson's catalyst gives the α -silyl nitriles in good yields (Eq. 298).⁴⁶⁶ The $\text{PhSiH}_3/\text{Mo}(\text{CO})_6$ combination reduces α,β -unsaturated nitriles to the nitriles in good yields, although the β,β -disubstituted 3-methylcrotonitrile does not react.⁴⁵⁰ Cinnamitrile is reduced to the saturated nitrile in good yield with PMHS/Pd -nanocomposite²¹⁹ and in only modest yield with $\text{Ph}_2\text{SiH}_2/\text{ZnCl}_2/\text{Pd}(\text{PPh}_3)_4$.⁴³⁶ The ferrocenyl unsaturated nitrile shown in Eq. 299 is reduced with $\text{Et}_3\text{SiH}/\text{TFA}$ in good yield.¹⁷⁹ The $\text{PhSiH}_3/\text{Co}(\text{dpm})$ reductive aldolizations of an α,β -unsaturated nitrile and an aldehyde also occur in good yields (Eq. 300).⁴⁷⁸

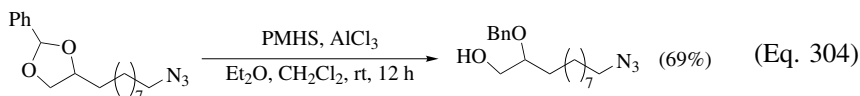
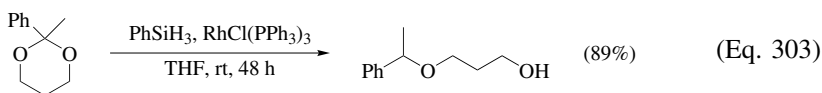


Reduction of Acetals, Ketals, Hemiacetals, Hemiketals, and Orthoesters

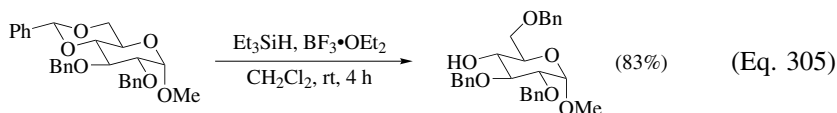
The ketals of both aryl and alkyl ketones can be reduced to the methylene derivatives in good yields (Eqs. 301 and 302).⁴⁷⁹



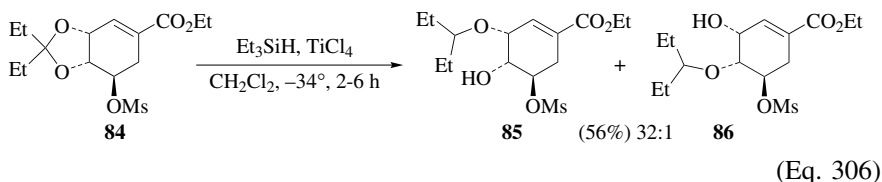
Simple dimethylacetals and ketals are reduced with the Et₃SiH/acid combination where the acid catalyst can be TMSOTf,^{339,480–482} BF₃•OEt₂,^{483–485} TFA,^{327,486} Nafion®-H,³³⁵ tin-montmorillonite,³⁵³ FSO₃H/BSA,⁴⁸⁷ TiCl₄,^{488–492} AlCl₃/HCl,¹⁴⁶ and FSO₃H/BSU.⁴⁸⁷ Of these, Nafion®-H, BF₃•OEt₂, BSA, and TMSOTf all give excellent isolated yields of the corresponding ether. The 1, 3-propanediol acetals of acetophenone and benzaldehyde are reduced to mono-ortho-benzylidiols with PhSiH₃/RhCl(PPh₃)₃ (Eq. 303),⁴⁹³ Et₃SiH/TFA,⁴⁹⁴ Et₃SiH/BF₃•OEt₂,⁴⁹⁵ or PMHS/AlCl₃ (Eq. 304).⁴⁹⁶



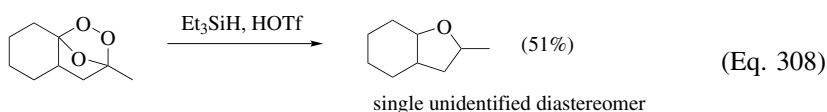
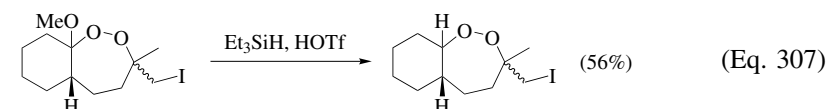
This reduction technique also applies to the benzaldehyde acetals of sugars with reduction of the benzaldehyde acetals taking place in preference to reduction of the anomeric acetal (Eq. 305).⁴⁹⁷



A highly useful and important regioselective reduction of substrate **84** leads to a mixture of 3-hydroxy ethers **85** and **86** in a 32 : 1 ratio (Eq. 306). Compound **85** is further converted to the anti-influenza drug oseltamivir phosphate, better known as Tamiflu®.⁴⁹⁸

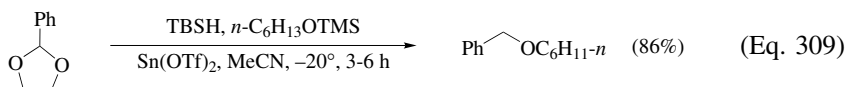


The triethylsilane reduction of the peroxy ethyl ether shown in Eq. 307 takes place at the C–O bond of the methyl ether without reduction of either the iodide or the peroxide functionalities (Eq. 307).⁴⁹⁹ In contrast, a bridged peroxy ether undergoes reduction of both C–O bonds of the peroxide linkage rather than at the ether bridge (Eq. 308).⁴⁹⁹

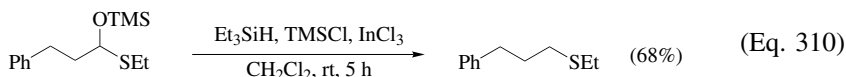


The Et₃SiH/tetracyanoethylene combination reduces acetals and ketals to the corresponding ethers but the yields are mixed.⁵⁰⁰ The full reduction of benzaldehyde acetals to the toluene derivatives is realized by the initial reduction with Et₃SiH/SnBr₂–AcBr followed by Bu₃SnH/AIBN (azobis(isobutyronitrile)) or LiAlH₄.⁴⁷⁹ The overall yields are excellent.

Diphenylmethylsilyl-protected hemiacetals are reduced upon treatment with Ph₂SiH₂/Mn(CO)₃Ac.²⁹⁵ Et₃SiH/TiCl₄ reduces *tert*-butyldimethylsilyl ketals.³⁰⁶ The combination of TBSH/Sn(OTf)₂ and a silyl ether converts ethylene glycol acetals and ketals into ethers (Eq. 309).⁵⁰¹

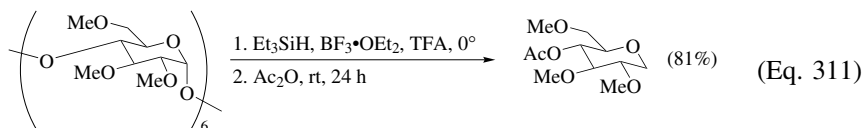


α -Trimethylsilyloxythianes are reduced to the respective thianes with Et₃SiH/TMSCl/InCl₃ (Eq. 310).^{426,502} Trimethylsilane with TMSI or TMSOTf effects this conversion as well.³⁹²

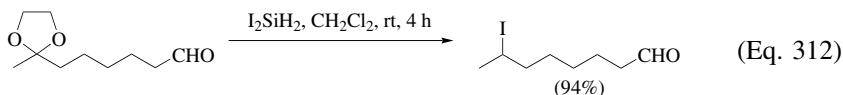


A number of conditions are available for the reduction of the anomeric acetals to the reduced sugars. Among these are the combinations Et₃SiH/BF₃•OEt₂/TFA⁴⁸³ and Et₃SiH/TMSOTf,^{503,504} although some isomerization is found to

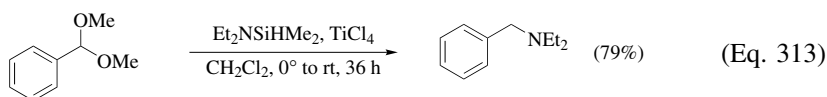
occur with this latter system. The polysaccharide shown in Eq. 311 is converted into the deoxysugar in good yield.⁴⁸³



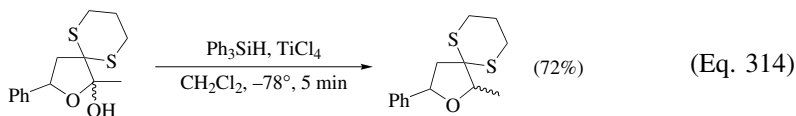
Diiodosilane reduces acetals to alkyl iodides in a reductive iodination reaction (Eq. 312).^{358,505} Alkyl bromides are formed from the reductive bromination of benzaldehyde acetals with the combination $\text{Et}_3\text{SiH}/\text{SnBr}_2$.⁵⁰⁶



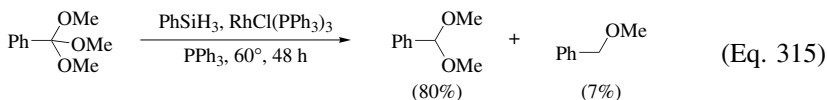
There is a report of a reductive amination of an acetal. Thus, $(\text{Et}_2\text{N})\text{Me}_2\text{SiH}/\text{TiCl}_4$ reacts with the dimethylacetal of benzaldehyde to form benzyldiethylamine in good yield (Eq. 313).³⁵⁹



Hemiacetals and hemiketals also undergo reduction to ethers with organosilanes under acid catalysis. These reductions generally occur in good yield. They are carried out with $\text{Et}_3\text{SiH}/\text{BF}_3\cdot\text{OEt}_2$,^{497,507–512} $\text{Et}_3\text{SiH}/\text{TFA}$,^{162,513–516} $\text{PhMe}_2\text{SiH}/\text{TMSOTf}$,⁵¹⁷ and $\text{Et}_3\text{SiH}/\text{TMSOTf}$,^{518,519} which prove especially useful for sugar systems. The combination of $\text{Ph}_3\text{SiH}/\text{TiCl}_4$ reduces hemiketals in the presence of a dithioketal (Eq. 314).⁵²⁰



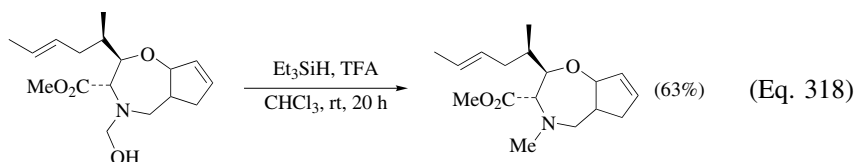
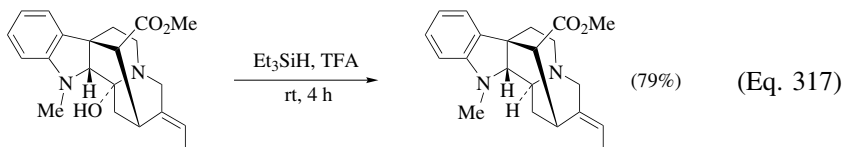
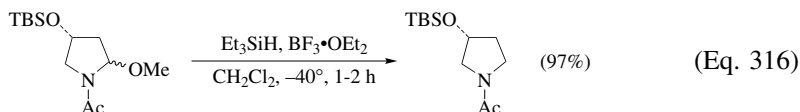
The $\text{PhSiH}_3/\text{RhCl}(\text{PPh}_3)_3$ combination reduces trimethyl orthobenzoate to the dimethyl acetal of benzaldehyde with small amounts of methyl benzyl ether product (Eq. 315).⁴⁹³



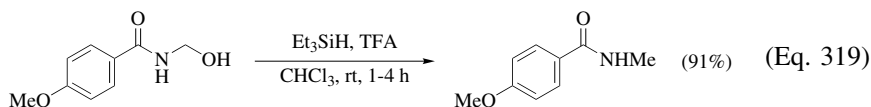
Reduction of Aminals and Hemiaminals

As demonstrated with acetals and ketals, aminals are also readily reduced with silanes under acid catalysis. The $\text{Et}_3\text{SiH}/\text{BF}_3\cdot\text{OEt}_2$ combination reduces

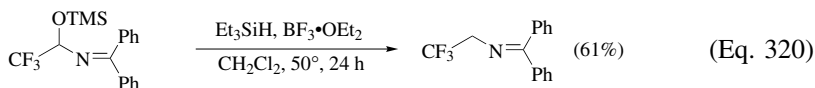
aminals to the amines in excellent yields (Eq. 316).^{521–523} A similar reduction with $\text{Et}_3\text{SiH/TFA}$ occurs in equally high yield (Eq. 317).⁵²⁴ Hemiaminals are reduced with $\text{Et}_3\text{SiH/TFA}$ (Eq. 318).⁵²⁵



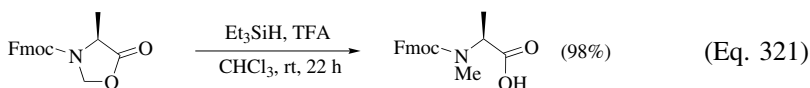
Amidoaminals and amidohemiaminals are reduced to the amides with organosilanes and an acid catalyst. Best among the reported reagent combinations are $\text{Et}_3\text{SiH/TiCl}_4$,⁵²⁴ and $\text{Et}_3\text{SiH/BF}_3\cdot\text{OEt}_2$.⁵²¹ $\text{Et}_3\text{SiH/TFA}$ ⁵²⁶ (Eq. 319) and $\text{Et}_3\text{SiH/BF}_3\cdot\text{OEt}_2$ ⁵²⁷ are effective in reducing amidoaminals in high yields.



N-Trimethylsilyloxymethylimines can be reduced to the corresponding *N*-alkylimines with $\text{Et}_3\text{SiH/BF}_3\cdot\text{OEt}_2$ (Eq. 320).⁵²²



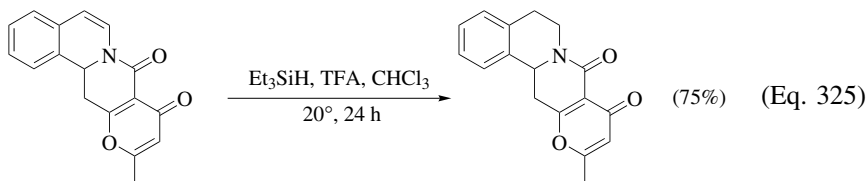
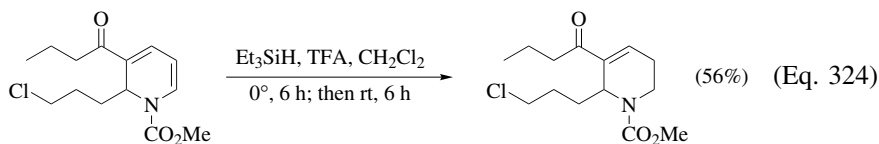
O-Aminomethyl lactones are reduced to amino acids with the $\text{Et}_3\text{SiH/TFA}$ combination (Eq. 321).⁵²⁸



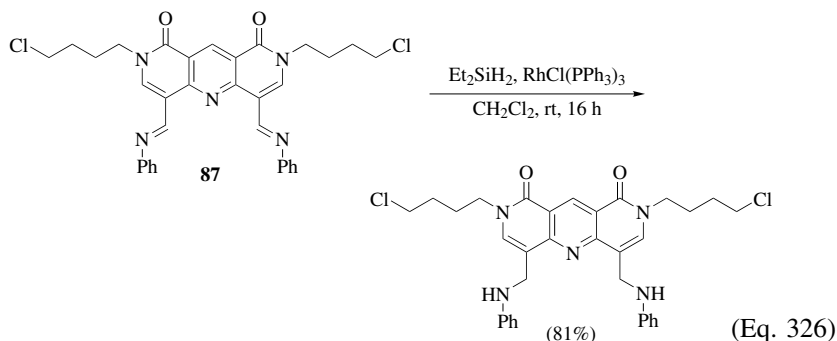
Reduction of Enamines

Enamines are reduced to amines in good yields with $\text{Et}_3\text{SiH/TFA}$.^{529–533} This reagent combination causes a variety of indoles to undergo stereoselective *cis*

The enamide double bond is reduced in preference over that of the enone moiety in each of the two examples shown below (Eqs. 324 and 325).^{536,537} Other enamides are reduced under similar conditions.^{235,537,538}

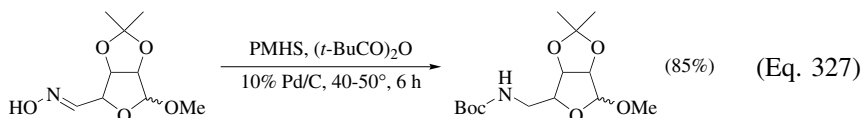


The reduction of imines with organosilanes is reported to take place with the reagent combinations PMHS/ZnCl₂,⁵³⁹ Et₃SiH/TFA,^{540,541} Cl₃SiH,^{318,542} PMHS/butyltin trioctanoate,⁵⁴³ PhSiH₃,⁵⁴⁴ Et₃SiH/HCO₂H,²⁰⁸ PhMe₂SiH/TFA,²⁷⁶ Cl₃SiH/BF₃·OEt₂,⁵⁴⁵ Et₃SiH (and related silanes)/RhCl(PPh₃)₃,⁵⁴⁶ and Cl₂SiH₂.⁵⁴⁵ Imines are reduced in high yields with various silanes in the presence of Wilkinson's catalyst or PdCl₂.¹²⁰ Triethylsilane and diethylsilane are the most effective reducing agents. Diimine **87** undergoes reduction of the imine functions with diethylsilane without reduction of the amide functionality, even though the amide carbonyl is in the more reactive α-heteroaryl position (Eq. 326).⁵⁴⁷

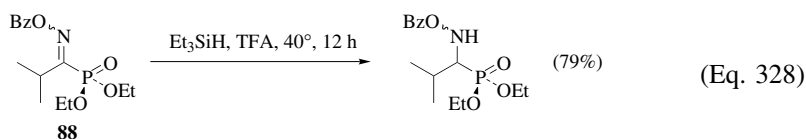


Reduction of Oximes

Oximes can be reductively converted into the Boc-protected primary amines in good yields with the combination of PMHS/(Boc)₂O/Pd/C (Eq. 327).⁵⁴⁸ *O*-Benzyloximes⁵⁴⁹ are reported to be reduced in good to excellent yields by this method.

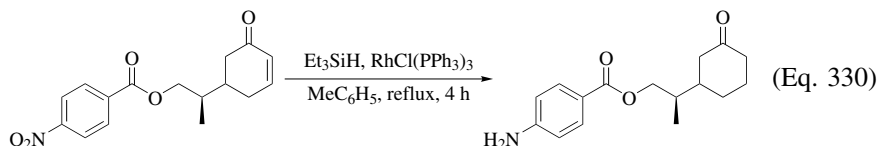
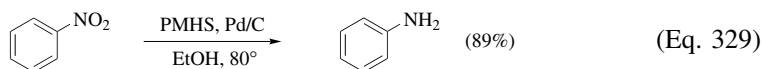


O-Benzyloximes are nicely reduced to *O*-benzoylhydroxylamines with Et₃SiH/TFA (Eq. 328).^{550,551} *O*-Acetyloximes are reduced with Et₃SiH/TMSOTf in moderate to high yields.⁵⁵² The diethylphosphatoimine **88** is reduced to the hydroxylamine derivative.⁵⁵³

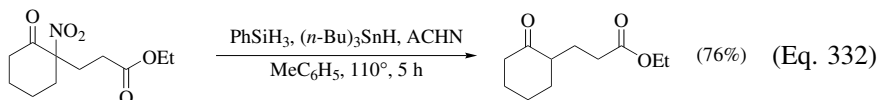
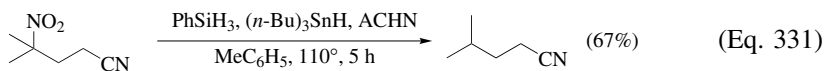


Reduction of Nitroalkanes

The combination PMHS/Pd/C reduces nitrobenzenes to anilines in high yields (Eq. 329),³¹⁶ as does Et₃SiH/RhCl(PPh₃)₃ (Eq. 330).⁵⁵⁴ This latter combination can also reduce both nitro and enone functionalities.⁵⁵⁴

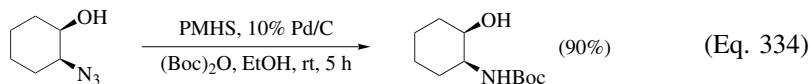
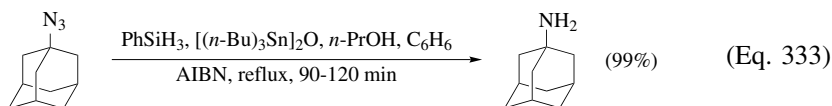


Tertiary nitro alkanes or activated nitro groups are reduced to the alkane with loss of the nitro group by a combination of PhSiH_3 and catalytic amounts of $(n\text{-Bu})_3\text{SnH}$ and 1,1'-azobis(cyclohexanecarbonitrile) (ACHN), even in the presence of other potentially reducible functional groups.⁵⁵⁵ The examples shown in Eqs. 331 and 332 illustrate this behavior.⁵⁵⁵

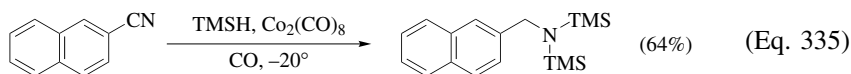


Reduction of Miscellaneous Nitrogen-Containing Compounds

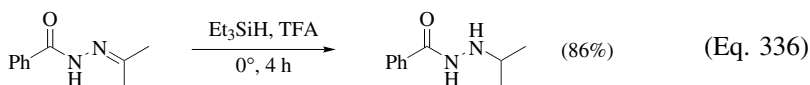
The combination of PhSiH_3 with a catalytic amount of bis(tri-*n*-butyltin) oxide reduces azides to primary amines in excellent yields (Eq. 333).⁵⁵⁶ The reducing agent is $(n\text{-Bu})_3\text{SnH}$ formed in situ by the silane. Azides are converted into Boc-protected primary amines with the PMHS/Pd/C reagent (Eq. 334).^{557,558}



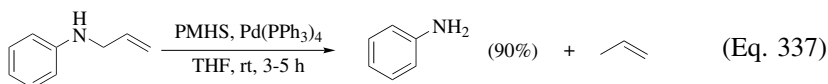
The combination of $\text{Et}_3\text{SiH}/\text{Co}_2(\text{CO})_8$ reduces nitriles to the *N,N*-bis(trimethylsilyl)amine (Eq. 335).⁵⁵⁹ These derivatives can be readily hydrolyzed to the primary amines.



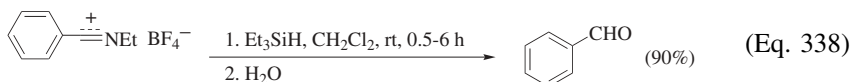
The organosilane reduction of hydrazones to hydrazines is readily accomplished in good yields with $\text{Et}_3\text{SiH}/\text{TFA}$ (Eq. 336).^{560,561} *N*-Tosylimines²⁹⁴ are reduced to their *N*-Boc tosylamino counterparts,²⁹⁴ and are also reduced with $(\text{MeO})_3\text{SiH}/\text{LiOMe}$ in good yields.²⁹⁴ Benzyl-protected hydroxylamines are reduced with $\text{PhMe}_2\text{SiH}/\text{TFA}$.⁵⁵¹



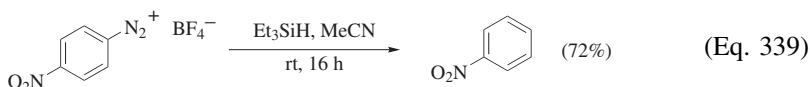
In an analogous fashion to the reductive deprotection of allyl alcohols and allyl esters, the deallylation of allylamines is also possible (Eq. 337).²⁷⁰



The tetrachloroferrate or tetrafluoroborate salts of alkylated alkyl- or aryl-nitriles (nitrilium ions) are reduced to imines with triethylsilane. Subsequent hydrolysis of the intermediate imines leads to aldehydes in good yields, thus providing an excellent overall route to aldehydes from nitriles (Eq. 338).^{28,562}

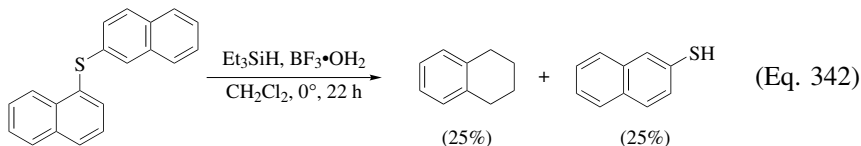
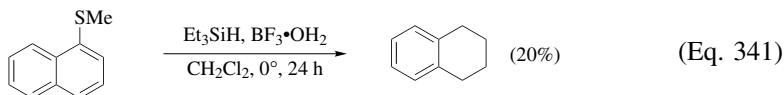
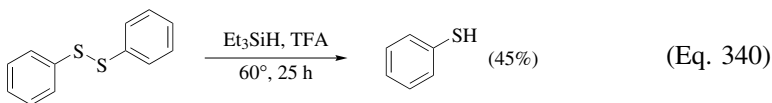


Aryldiazonium salts are reduced to the benzene derivatives in good yields (Eq. 339).⁵⁶³

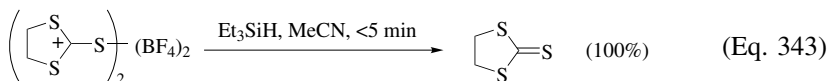


Reduction of Miscellaneous Sulfur-Containing Compounds

Et₃SiH/TFA reduces disulfides to the corresponding mercaptans in modest yields (Eq. 340).⁵⁶⁴ Naphthyl thio ethers are reduced in rather poor yields to tetrahydronaphthalene with the combination Et₃SiH/BF₃•OH₂ (Eq. 341).²⁶³ There is one report of the reduction of a diaryl sulfide to the hydrocarbon but the yield is low (Eq. 342).²¹⁷

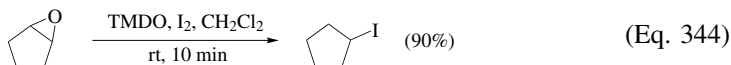


The reduction of 2,2'-dithiobis(1,3-dithiolanium) bis(tetrafluoroborate) to the thiocarbonate compound by triethylsilane takes place quantitatively (Eq. 343).⁵⁶⁵

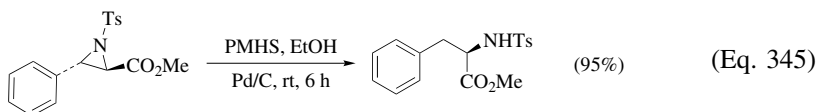


Reduction of Small-Ring Heterocycles

The reduction of epoxides occurs with the reagent combinations $\text{Et}_3\text{SiH}/\text{BF}_3$ ⁵⁶⁶ and $\text{Et}_3\text{SiH}/\text{BF}_3\cdot\text{OEt}_2$.⁴⁰⁷ The reductive iodination of epoxides is carried out with the combination of TMDO and iodine (Eq. 344).³⁵⁷ The yields are good to excellent. The reductive bromination of epoxides is accomplished in a similar manner. Trimethylchlorosilane is found to enhance these reactions.⁵⁶⁷



N-Tosylaziridines are reduced with the combination PMHS/Pd/C in ethanol to yield the ring-opened *N*-tosyl primary amines (Eq. 345).⁵⁶⁸

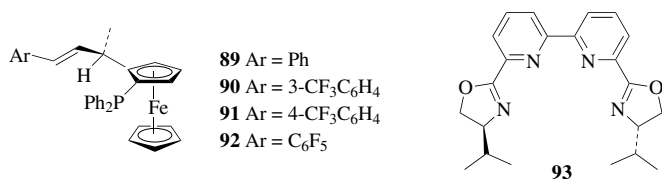


Asymmetric Reduction of Ketones

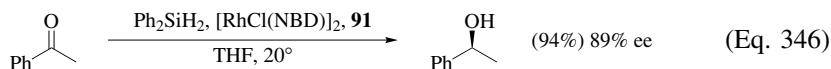
The asymmetric organosilane reduction of prochiral ketones has been studied as an alternative to the asymmetric hydrogenation approach. A wide variety of chiral ligand systems in combination with transition metals can be employed for this purpose. The majority of these result in good to excellent chemical yields of the corresponding alcohols along with a trend for better ee results with aryl alkyl ketones than with prochiral dialkyl ketones.

Oxazolinylferrocenylphosphines complexed *in situ* with $\text{RuCl}_2\text{PPh}_3$ is one system used to catalyze the diphenylsilane reduction of prochiral ketones.^{569–571} The best results are obtained when AgOTf or $\text{Cu}(\text{OTf})_2$ is employed as an additive. Although the chemical yields are modest, the ee values range from 43% (methyl cyclohexyl ketone) to 97% (propiophenone). Chiral bis(oxazolinyl)bipyridine (bipymox) ligands in combination with rhodium(II) chloride, AgBF_4 , and diphenylsilane reduce prochiral ketones in good to excellent yields and 24 to 90% ee.⁵⁷² The complexes formed with rhodium(I) are not as effective and some silyl enol ethers are formed from enolizable ketones. Rhodium(I) complexes with (+)- or (–)-DIOP [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)bis(diphenylphosphine)] ligands catalyze the diphenylsilane reduction of 17-keto steroids with only a moderate enhancement for the α -hydroxy steroid over the results obtained from the corresponding achiral reductions.⁵⁷³

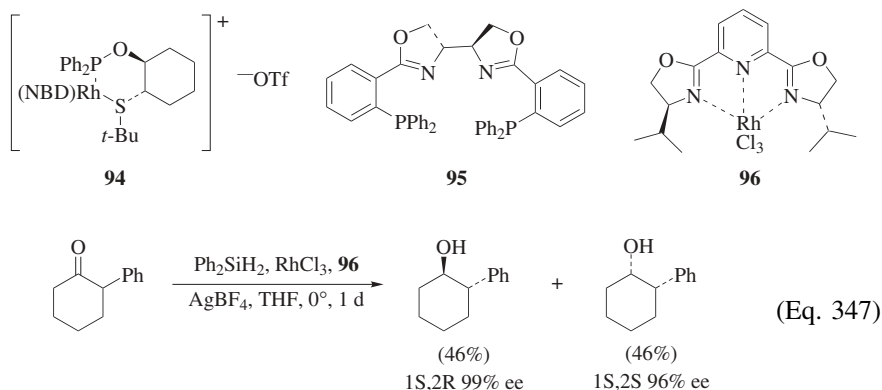
The combination of $[\text{Rh}(\text{Cl}(\text{NBD}))_2]$ and ligands **89**, **90**, **91**, or **92** with diphenylsilane asymmetrically reduces aryl alkyl ketones, including acetophenones, in excellent yields and in 81 to 90% ee (Eq. 346).⁵⁷⁴ The best results are with ferrocene **91** and acetophenone in toluene.⁵⁷⁵ Other phosphine-substituted ferrocenes do not give comparable results. Rhodium(I) complexes of TADDOL-derived



phosphates containing a chiral dihydrooxazole unit such as **93** are also used to catalyze the diphenylsilane reduction of prochiral ketones.

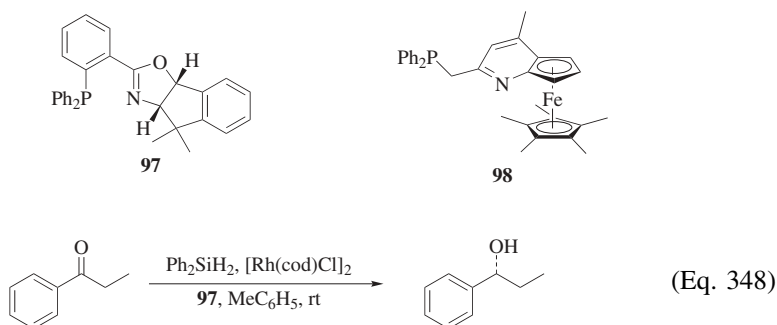


The combination of 1-naphthylphenylsilane and a rhodium(I) catalyst derived from Evans' mixed phosphine/sulfur ligands, for example **94**, reduces acetophenone in 95% ee. Other aryl alkyl ketones are reduced with similarly excellent ee values.⁵⁷⁶ Under similar conditions, dialkyl ketones and β -keto esters are reduced in good yields and moderate to excellent ee. The asymmetric reduction of aryl alkyl ketones with diphenylsilane is accomplished with excellent ee values through the use of a rhodium(I) complex with TRAP (2,2'-bis[(dialkylphosphino)methyl]-1,1'-biferrocene) ligands.^{577,578} These systems are also successful for the 1,2 asymmetric reduction of α,β -unsaturated ketones. The (*S,S*)-Phos-Biox ligand **95**, when complexed with rhodium(I), provides a catalyst that can be used in the diphenylsilane reduction of acetophenones to give the corresponding R-configured alcohols in high yields and >90% ee.⁵⁷⁹ The complex **96** is highly successful in the diphenylsilane reduction of aryl alkyl ketones with high yields and >90% ee values.^{580,581} Dialkyl ketones are reduced with more mixed results, with 2-octanone showing 63% ee and ethyl 4-oxopentanoate 95% ee. The same system can be used to reduce 2-phenylcyclohexanone with no cis/trans selectivity, but excellent enantioselectivity (Eq. 347).³⁹⁰



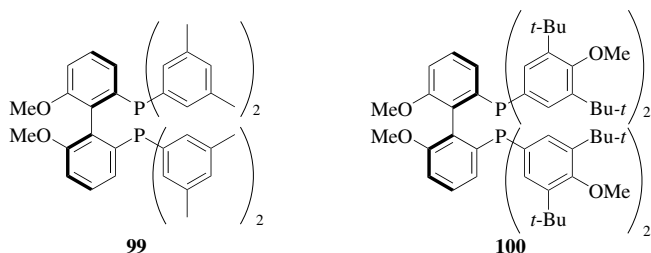
A chiral oxazolinoferrocene ligand with iridium(I) is used for the diphenylsilane reduction of aryl alkyl ketones in nearly quantitative yields and >83% ee

values.⁵⁸² The dialkyl ketone, 2-octanone, is reduced with a poor 19% ee under these conditions. A catalyst prepared by the alkylation of [1,2-bis(tetrahydroindenyl)ethane]titanium(IV) 1,1'-binaphth-2,2'-diolate with methyllithium or *n*-butyllithium can be employed in the methyldiethoxysilane reduction of acetophenone with 99% ee.^{583,584} Other ketones do not show nearly the same ee values. Methylsilane is the actual proposed reducing agent in this system. The phosphinophenylloxazoline **97** is an effective ligand for the asymmetric rhodium(I) diphenylsilane reduction of aryl alkyl ketones, even with propiophenone, which has proven difficult with other systems, showing 91% ee and 91% yield (Eq. 348).⁵⁸⁵ A more general system involving mesitylphenylsilane and catalyst **98** permits the reduction of aryl alkyl ketones in very high chemical yields and >96% ee.⁵⁸⁶ The reduction of dialkyl ketones ranges from 72% ee for 2-octanone to 96% ee for the more stereo-differentiated adamantly methyl ketone.

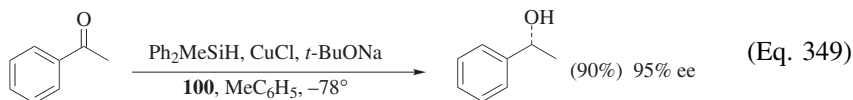


Alkylated (*R,R*)-tetrahydroindenyltitanium difluoride and phenylsilane serve to asymmetrically reduce a variety of ketones, especially aryl alkyl ketones, in excellent chemical yields and >96% ee.⁵⁸⁷ The use of the easier to handle and less expensive PMHS is also highly effective in these transformations. In a related study using the (*R,R*)-tetrahydroindenyltitanium 1,1'-binaphth-2,2'-diolate precursor to the active catalyst, similarly impressive results are obtained.⁵⁸⁸

The in situ generation of CuH from organosilanes in the presence of either a BIPHEP (**99**) or a SEGPHOS (**100**) type ligand represents a general method for the asymmetric hydrosilylation of aryl alkyl ketones at low temperatures.

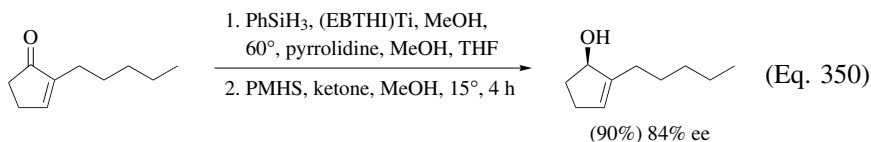


These excellent catalyst systems show high reactivity, substrate-to-ligand ratios of $>100,000:1$, high chemical yields, the ability to employ the inexpensive PMHS as the hydride donor, and typical ee values in the $>90\%$ range.^{589,590} The most promising ligand found to date is DTBM-SEGPHOS (5,5'-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole) **100** (Eq. 349). The BIPHEP ligand with copper(I) is also capable of asymmetrically reducing aryl alkyl ketones under similar conditions and with comparable results.^{589,591}

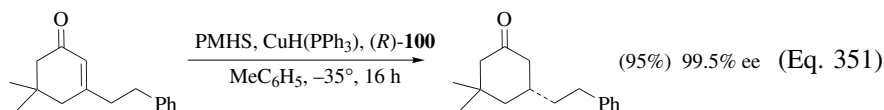


Asymmetric Reduction of α,β -Unsaturated Ketones

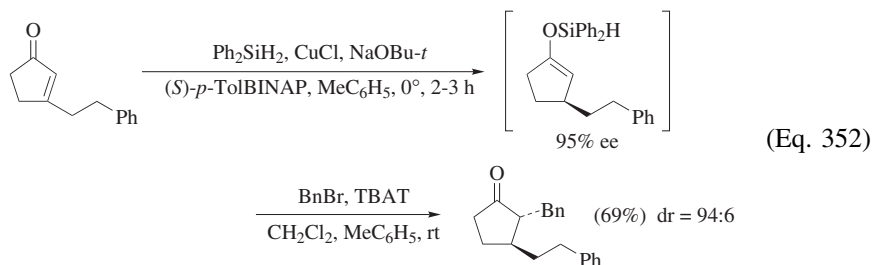
The enantioselective hydrosilylation of 2-pentylcyclopentenone is effected with PMHS and an active catalyst derived from (*R,R*)-ethylenebis(tetrahydroindenyl)titanium difluoride and phenylsilane (EBTHI)Ti (Eq. 350).⁵⁸⁷ The use of diphenylsilane, a rhodium catalyst, and (*R,R*)-(*S,S*)-BuTRAP as the chiral ligand gives similar results.⁵⁷⁶ Other related approaches give greatly inferior enantioselectivities.^{592–594}



The PMHS, copper-catalyzed reduction of β -substituted α,β -unsaturated ketones to saturated ketones is accomplished in good yield with ee values in the 90 to 95% range when (*S*)-*p*-Tol-BINAP is employed as the chiral ligand.^{595,596} Higher ee values are achievable with the use of a copper catalyst and (*R*)-**100** as the chiral ligand (Eq. 351).⁵⁹⁷

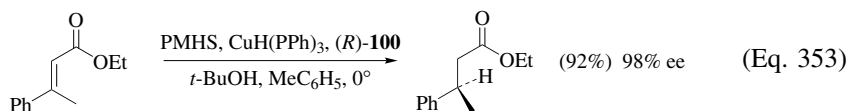


The sequence of chiral 1,4-reduction of a β -substituted cyclopentenone followed by electrophilic trapping of the intermediate enolate provides an efficient route to chiral 2,3-disubstituted cyclopentanones that generates two chiral centers in the process (Eq. 352).⁴⁵⁹

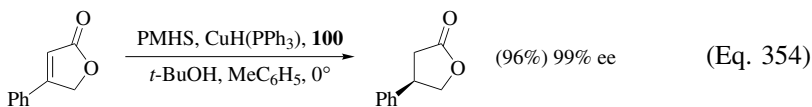


Asymmetric Reduction of α,β -Unsaturated Esters and Lactones

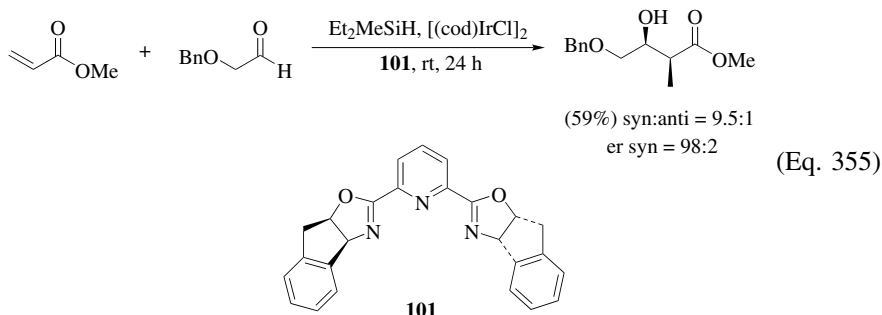
The chiral hydrosilylation of β -substituted α,β -unsaturated esters to their saturated counterparts is the subject of reports by two groups. The combination of triphenylphosphinecopper hydride and (R) -DTBM-SEGPHOS is reported to give excellent yields of the β -substituted esters (Eq. 353).⁵⁹⁸ Comparable yields, but with lower ee values, are reported for this transformation.^{599,600}



The copper-catalyzed chiral reduction of β -substituted α,β -unsaturated lactones with PMHS and (S) -*p*-Tol-BINAP in the presence of a hindered alcohol can be carried out in moderate to good yields with moderate ee values.⁵⁹⁹ The reaction is useful for both butenolides and pentenolides. Inferior results are realized with diphenylsilane as the reducing agent. Excellent results employing PMHS and the DTBM-SEGPHOS ligand are possible (Eq. 354).⁵⁹⁸

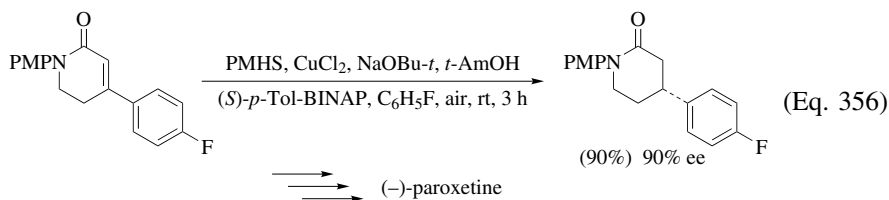


The asymmetric reductive rhodium- and iridium-catalyzed aldol reaction of α,β -unsaturated esters with aldehydes^{470,601,602} is proposed to involve a rhodium(I) or iridium(I) hydride as the active catalyst, which adds to the α,β -unsaturated ester, followed by reaction of the intermediate rhodium or iridium enolate with an aldehyde.⁴⁷⁰ These transformations provide an excellent entry into α -alkyl- β -hydroxy esters in both high yields and high enantiomeric ratios. The reactions were first carried out with moderate success using the BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) ligand to introduce the asymmetry.^{470,603} The use of various pybox ligands improves the yields of these transformations.⁶⁰⁴ The best results are obtained from the ligand indane-pybox (**101**) and an iridium catalyst,⁶⁰⁴ which was applied to an enantioselective synthesis of the macrocycle borrelidin (Eq. 355).^{601,602}



Asymmetric Reduction of α,β -Unsaturated Lactams

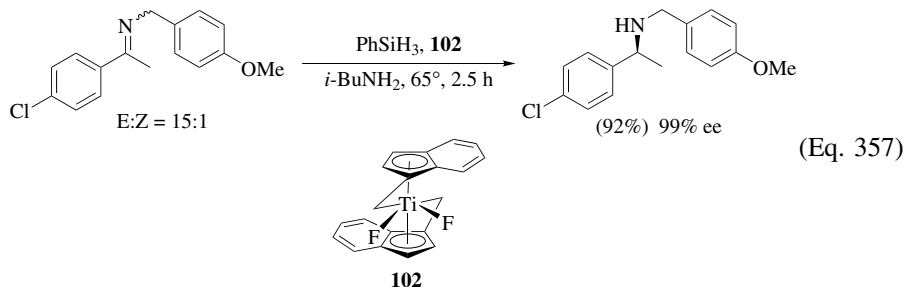
The chiral reduction of β -substituted α,β -unsaturated lactams with PMHS in the presence of (*S*)-*p*-Tol-BINAP as the chiral ligand with a copper catalyst results in β -substituted lactams in excellent yield and with greater than 90% ee.⁵⁹⁹ This method has been applied in an efficient enantioselective synthesis of the antidepressant (–)-paroxetine (Eq. 356).



Asymmetric Reduction of Imines

Various chiral ligands with metal catalysts can be employed in the organosilane reduction of imines to amines. Many of these provide modest success. These include (oxazolino)diphenylphosphinoferrocene ligands with ruthenium,⁶⁰⁵ (–)-DIOP/Rh(I),^{606,607} 3,3'-BINOL (1,1'-bi-2-naphthol) and LiHMDS,⁶⁰⁸ and (*S*)-phenyl *N*-formylprolinamide with trichlorosilane.⁶⁰⁹

Some excellent findings in the asymmetric organosilane reduction of both aryl alkyl and dialkyl imines have resulted in the development of practical, scaleable methodologies for this key transformation. The reduction of imines with the ethylenebis(η^5 -tetrahydroindenyl)titanium (EBTHI)–TiF₂-derived catalyst **102** with either phenylsilane or PMHS as the reducing agent gives high chemical yields of the corresponding amine and ee values well in excess of 90% with most at 99% (Eq. 357).^{610–613} Straight-chain dialkyl imines are not as successful; for example, 2-(*N*-benzylimino)octane gives a 96% yield of (*S*)-(2-benzylamino)octane with 69% ee.⁶¹² The CuH approach employed so successfully for the asymmetric organosilane reduction of ketones can be applied with equal success to the reduction of phosphoryl imines, thus providing a route to the asymmetric reduction of imines to primary amines via the hydrolysis of the resulting aminophosphorane.^{598,614}

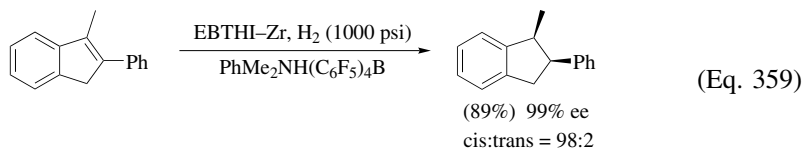
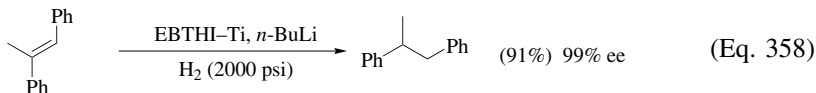


COMPARISON WITH OTHER METHODS

Many different methods are known and used for the reduction of organic functional groups. These have been reviewed many times over the years and are too numerous to repeat here. The sequence of hydrosilylation of a multiple bond followed by removal of the silyl group is tantamount to the addition of hydrogen. Coupled with the keen current interest in asymmetric reductions, the use of hydrogen in asymmetric reductions and related reactions is highlighted here. The numerous asymmetric hydrogenations and asymmetric reductions with metal hydrides, including lithium aluminum hydride, sodium borohydride, and borane, coordinated or reacted with chiral diols, amino alcohols, diamines, and variations of these have been extensively reviewed.^{615–631} In view of the very large number of methods for the reduction of organic functional groups and the high interest in asymmetric reductions, the choice of competitive examples is limited to those that are representative of asymmetric hydrogenations.

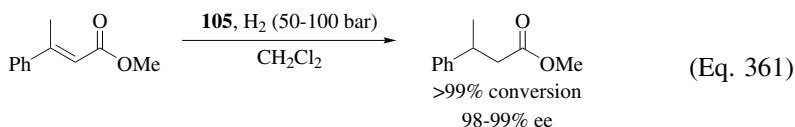
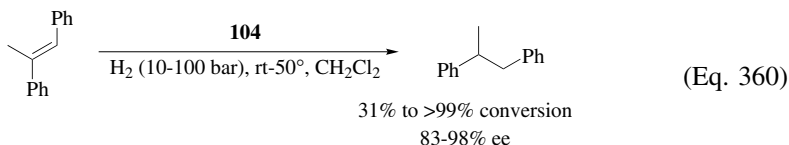
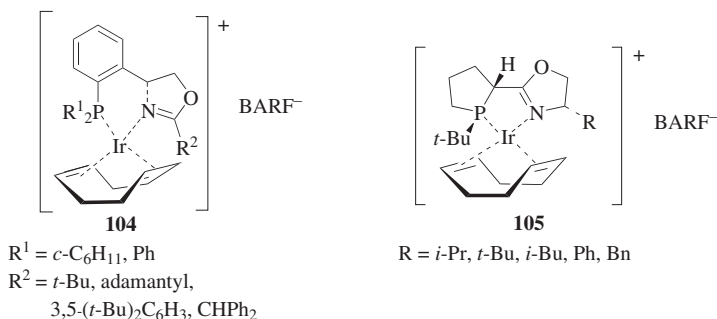
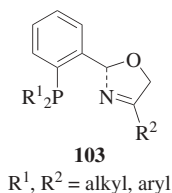
Asymmetric Hydrogenation of Olefins

EBTHI–Ti, when treated with *n*-BuLi, catalyzes the hydrogenation of trisubstituted olefins in good yields and excellent enantioselectivity though undetermined configuration (ee = 83% to >99%) (Eq. 358)⁶³² A zirconium version of this approach is also successful in the asymmetric hydrogenation of terminal olefins, although the enantioselectivities are not high.⁶³³ On the other hand, this system gives excellent ee values when applied to the hydrogenation of disubstituted cyclic olefins (Eq. 359)⁶³⁴



Chiral phosphinodihydrooxazole iridium ligands are used to hydrogenate trisubstituted olefins in moderate yields and high enantioselectivity albeit of

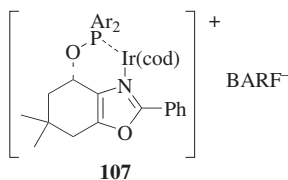
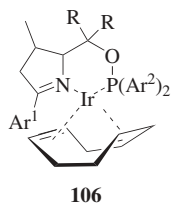
undetermined configuration.⁶³⁵ In a similar fashion and with equally impressive results, phosphine-oxazoline complexes of iridium **104**, derived from $[\text{Ir}(\text{cod})\text{Cl}]_2$ and **103**, are able to catalyze the hydrogenation of stilbenes (Eq. 360) and β -methyl cinnamic esters with both excellent conversion and enantioselectivity of undetermined configuration.⁶³⁶ The complex **105** also gives excellent results (Eq. 361).⁶³⁷



The asymmetric hydrogenation of trisubstituted olefins with iridium complexes of chiral phosphinite-oxazoline ligands of the general structure **106** also provides excellent results with ee values in the 85–99% range.⁶³⁸ The asymmetric hydrogenation of imines with these systems gives only moderate results. A similar fused phosphinite-oxazoline iridium catalyst, **107**, gives good results with 1,1-disubstituted and trisubstituted olefins with ee values of >97%, although ethyl β -methylcinnamate gives poor results.⁶³⁹

Asymmetric Hydrogenation of Ketones

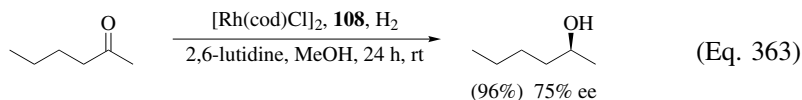
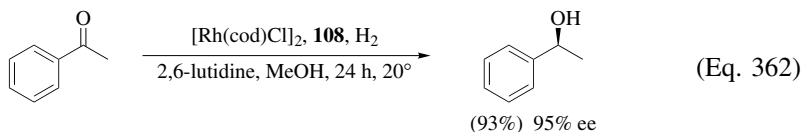
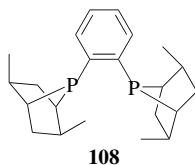
A number of asymmetric hydrogenations of prochiral ketones to highly enantiomerically enriched alcohols are available. A select few are highlighted here.



R	Ar ¹	Ar ²
Bn	Ph	Ph
Bn	Ph	2-MeC ₆ H ₄
Me	Ph	Ph
Bn	3,5-Me ₂ C ₆ H ₃	Ph
Bn	3,5-(<i>t</i> -Bu) ₂ C ₆ H ₃	Ph

Ar = Ph, 2-MeC₆H₄

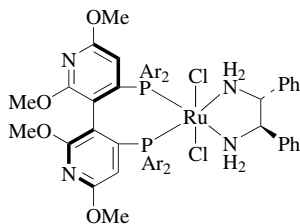
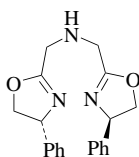
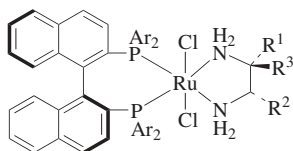
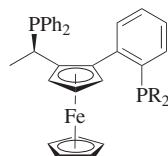
The PennPhos ligands, for example **108**, complexed with rhodium, provide an excellent system for the hydrogenation of aryl alkyl ketones with ee values in the range of 94–96% (Eq. 362). Phenyl isopropyl ketone shows only a 72% ee under similar conditions. Dialkyl ketones exhibit ee values in the range of 73–94% with this system (Eq. 363).⁶⁴⁰



Enantioselectivities in the range of 97.7–99.9%, with the majority in the range of 98.4–99.1%, are obtained in the asymmetric hydrogenation of aryl alkyl ketones with ruthenium catalyst **109**.⁶⁴¹ The same systems can hydrogenate β -keto esters (95.2–98.6% ee) and α,β -unsaturated acids (96.2% in a single example).⁶⁴²

Asymmetric transfer hydrogenation can be employed in the asymmetric hydrogenation of prochiral ketones with a ruthenium complex of bis(oxazolinylmethyl) amine ligand **110**. Enantioselectivities are greater than 95%.⁶⁴³

The BINAP system of general structure **111** can be used in asymmetric hydrogenations; the compound in which Ar = 3,5-Me₂C₆H₃, R¹ = R² = 4-MeOC₆H₄,

**109**Ar = Ph, 4-MeC₆H₅, 3,5-Me₂C₆H₃**110****111****112**

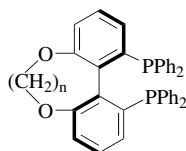
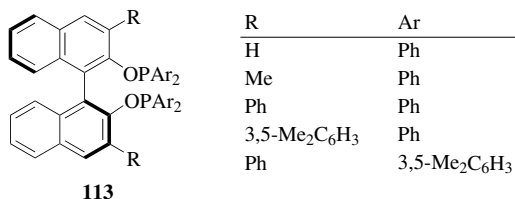
Ar	R ¹	R ²	R ³
3,5-Me ₂ C ₆ H ₃	4-MeOC ₆ H ₄	<i>i</i> -Pr	4-MeOC ₆ H ₅
3,5-Me ₂ C ₆ H ₃	—(CH ₂) ₄ —	H	H
3,5-Me ₂ C ₆ H ₃	Ph	Ph	H

R
<i>c</i> -C ₆ H ₁₁
<i>t</i> -Bu
3,5-Me ₂ -4-MeOC ₆ H ₂
Ph
3,5-(CF ₃) ₂ C ₆ H ₃

and R³ = *i*-Pr effects the asymmetric hydrogenation of cyclopropyl methyl ketone (95% ee), cyclopropyl phenyl ketone (96% ee), and other aryl alkyl ketones (94 to 100% ee), and is also useful for the 1,2-reduction of enones (>90% ee).⁶⁴⁴ 2,4-Pentanedione is hydrogenated to the 2-(*R*)-4-(*R*)-2,4-pentanediol in 97% ee with ligand **112** and [RuI₂(*p*-cymene)]₂. This system gives a wider range of enantioselectivity with prochiral ketones (22–97% ee) and α,β -unsaturated acids and esters (8–95% ee).⁶⁴⁵

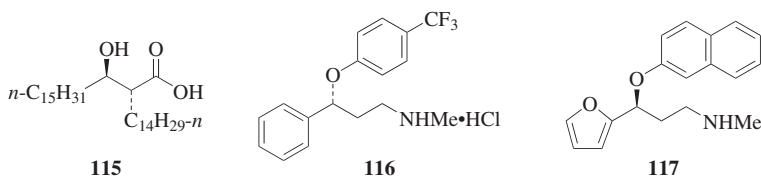
o-BINAPO ligands of the type **113** complexed with ruthenium give good enantioselectivity in the hydrogenation of β -keto esters with the more hindered ortho-substituted aryl substituents giving the best results.⁶⁴⁶ The selectivities range from 87–99% ee. These same systems hydrogenate the double bond of β -amido acrylates in >90% ee.

The TunaPhos ligands of general structure **114**, when complexed with [RuPhCl]₂, bring about the asymmetric hydrogenation of β -keto esters with

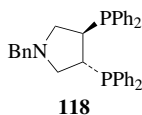


high ee values. The results compare very favorably with those obtained with (*R*)-BINAP and (*R*)-BIPHEP. The best results are found where $n = 4$, which gives a dihedral angle of the phosphines of 88 degrees.⁶⁴⁷

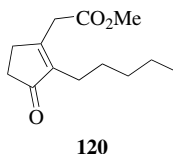
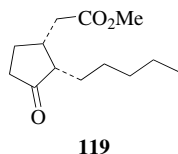
(*R*)-BINAP-RuBr₂ can be successfully applied to the enantioselective hydrogenation of β -keto esters in the synthesis of (+)-(2*R*,3*R*)-corynomycolic acid **115**. (*S*)-MeO-BIPHEP-RuBr₂ was used in a similar manner in the synthesis of (*R*)-fluoxetine (**116**, Prozac®) and (*S*)-duloxetine (**117**).⁶⁴⁸



The highly enantioselective reductive amination of α -keto acids as a route to amino acids is possible with ligand **118** [(3*R*,4*R*)-1-(*N*-benzyl)-3,4-bis(diphenylphosphanyl)pyrrolidine, DEGUPHOS] and [Rh(cod)₂]BF₄.⁶⁴⁹ (*R,R*)-NORPHOS (2-exo-3-endo-bis(diphenylphosphino)bicyclo[2.2.1]heptene) and (2*S*,3*S*)-CHIRAPHOS (bis(diphenylphosphino)butane) are also good ligands for this transformation. Arylpyruvic acids give the best results (>95% ee).



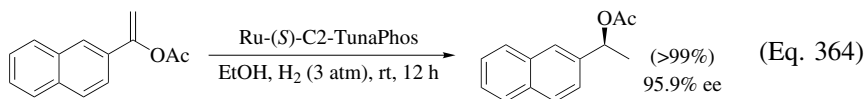
The industrially important cis-(+)-methyl jasmonate **119** is conveniently prepared by the hydrogenation of enone **120** with Me-DuPHOS and [Ru(1,2:5,6- η -cod)(η^3 -methallyl)]₂.⁶⁵⁰



(*S*)-C₃-TunaPhos (1,13-bis(diphenylphosphino)-7,8-dihydro-6*H*-dibenzo[*f,h*][1,5]dioxonin) ruthenium catalyzes the hydrogenation of α -phthalimido ketones with enantioselectivities of >94%,⁶⁵¹ leading to a highly enantioselective route to β -aminoethanols.

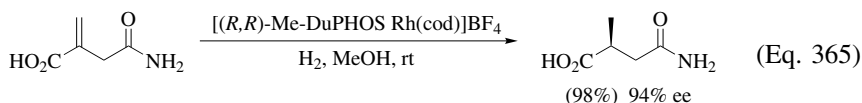
Asymmetric Hydrogenation of Enol Acetates

The diphosphine ligand **108** is useful in the asymmetric hydrogenation of enol acetates to chiral acetates, with 80.9% to >99% ee values being realized.⁶⁵² The ruthenium TunaPhos complexes from ligand **114** catalyze the asymmetric hydrogenation of enol acetates with high enantiomeric excesses (Eq. 364).⁶⁵³ High yields and high ee values are obtained via hydrogenation of enol acetates with an achiral ruthenium catalyst and a lipase.⁶⁵⁴ This same system is used to convert prochiral ketones into chiral acetates with high enantiomeric excess.

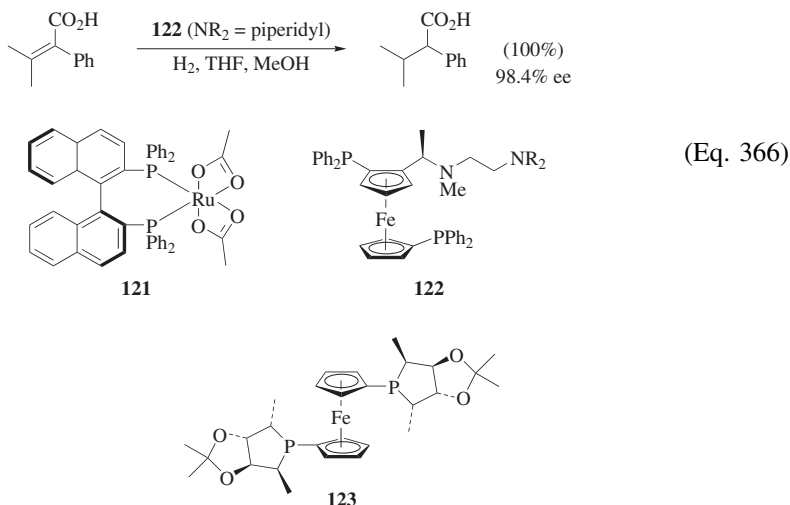


Asymmetric Hydrogenation of α,β -Unsaturated Acids

A study of various diphosphine ligands with rhodium catalyst systems for the hydrogenation of 2-methylenesuccinamic acid favors the DuPHOS (substituted 1,2-bis(phospholano)benzene) Rh(I) and Et-ferroTANE[®] (1,1'-bis-2,4-diethylphosphotano)ferrocene) Rh(I) systems, with the former being slightly better than the latter (Eq. 365).⁶⁵⁵ The conversions are high for both systems. BINAP-ruthenium complexes are successful in the asymmetric hydrogenation of α,β -unsaturated acids, with catalyst **121** showing the best results of those complexes studied.⁶⁵⁶ The chiral diaminoferrocenediphosphine ligand **122** catalyzes the reduction of trisubstituted acrylic acids with ee values of >92% (Eq. 366).⁶⁵⁷

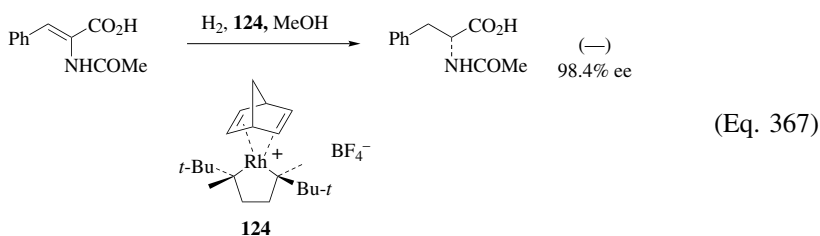


Itaconic acids are reduced in very high enantiomeric excesses (>97%) with Rh-TangPhos catalysts.⁶⁵⁸ Itaconic acid is reduced in 99.5% ee with the sugar-derived ferrocenyl phosphine **123**.⁶⁵⁹



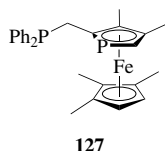
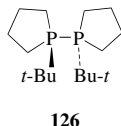
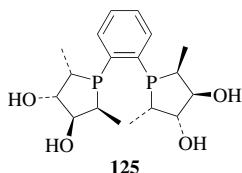
Asymmetric Hydrogenation of Acetamidoacrylates

The understandably strong interest in the synthesis of highly enantiomerically enriched α - and β -amino acids has made the asymmetric hydrogenation of α - and β -acetamidoacrylates an active area of investigation. The catalyst Rh-TangPhos catalyze the reduction of β -aryl- α -acetamidoacrylates with high enantioselectivity (>99% and >97%, respectively).⁶⁶⁰ Chiral norbornadienyl diphosphoryl rhodium(I) complexes of the type **124** catalyze the asymmetric hydrogenation of α -acetamidoacrylates with high ee values (Eq. 367).⁶⁶¹ Rhodium(I) trap complexes catalyze the hydrogenation of the α -acetamidoacrylates with ee values in the 80–88% range.⁶⁶²

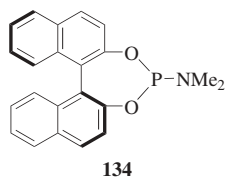
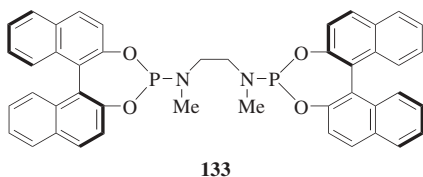
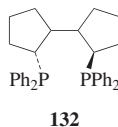
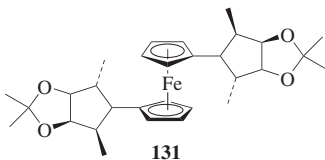
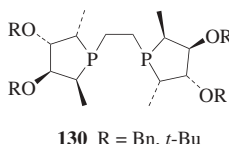
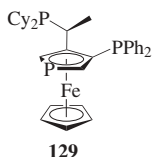
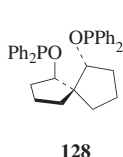


The rhodium(I) complexes with hydroxyphospholane ligand **125**⁶⁶³ or **126**⁶⁶⁰ catalyze the asymmetric hydrogenation of α -acetamidoacrylates with ee values in excess of 98%. System **125** is also very effective in the asymmetric hydrogenation of β -acetamidoacrylates (up to 99.6% ee).⁶⁶⁴ The planar-chiral heterocyclic ligand **127** complexed with rhodium(I) catalyzes the hydrogenation of α -acetamidoacrylates in excellent yields and ee values from 79–96% under mild conditions.⁶⁶⁵

Other systems that prove successful in the highly enantioselective hydrogenation of α -acetamidoacrylates include the spirophosphinites **128** (94.2–97.2% ee)⁶⁶⁶ and the Josiphos ligands **129** with rhodium(I) (84–96% ee). Excellent



results are also obtained with dimethyl itaconate and styrenes.⁶⁶⁷ The bis (phospholanes) of type **130**, again with rhodium(I), catalyze the hydrogenation of α -acetamidoacrylates in 92.6–99.1% ee.⁶⁶⁸ The ligands **131**,⁶⁵⁹ **132**,⁶⁶⁹ **133**,⁶⁷⁰ and **134**⁶⁷⁰ all show good results in the asymmetric hydrogenation of α -acetamidoacrylates, with **131** being especially effective, often rendering ee values of $>99.9\%$.

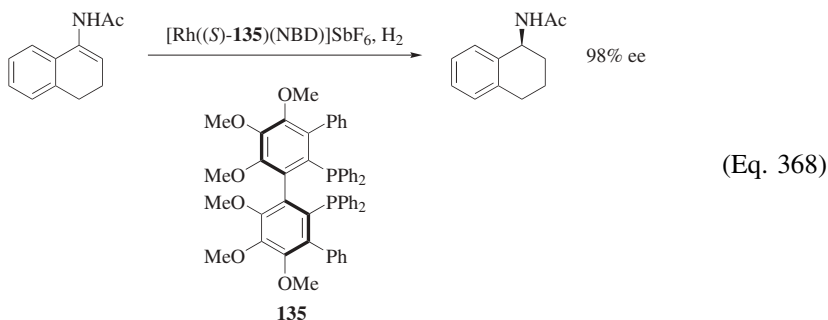


The various TunaPhos ligands with ruthenium(0) all catalyze the asymmetric hydrogenation of 2-acetylaminocyclopent-1-enecarboxylic acid ethyl ester in $>99\%$ ee.⁶⁷¹ The larger ring sizes give lower ee values. Good results are obtained in the asymmetric hydrogenation of β -acetamidoacrylates with the Et-ferroTANE[®] rhodium(I) complex.⁶⁷² The Rh-TangPhos catalyst system brings about the hydrogenation of α -aryl- β -substituted enamides with high enantioselectivity.⁶⁶⁰

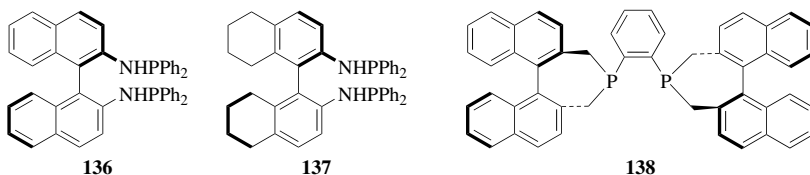
Asymmetric Hydrogenation of Enamides

Enamides, in addition to the acrylates shown above, are also asymmetrically hydrogenated with many of the same systems that prove useful for the acetamidoacrylate reductions. The Rh(I)/BICP (2(*R*)-2'(*i*)-bis(diphenylphosphino)-1(*R*),1'(*R*)-dicyclopentane) **132** and Rh(I)/DuPHOS systems work well ($>90\%$ ee) for the asymmetric hydrogenation of β -acetamidovinyl methoxymethyl ethers

in an approach to enantiomerically enriched β -aminoethanols.⁶⁷³ The Rh-binaphane system **138** catalyzes the reduction of aryl alkyl enamides in up to 99.6% ee.⁶⁷⁴ Cyclic enamides are reduced in 37–99% enantiomeric excess with the Rh(I)/**135** system (Eq. 368).⁶⁷⁵



The Rh(I)/**136** or Rh(I)/**137** combination can be used in the asymmetric hydrogenation of 1-arylenamides in 90–99% ee, with Rh(I)/**137** being the better of the two.⁶⁷⁶ Me-DuPHOS and related ligands with rhodium(I) reduce 1-aryl-2-alkylenamides in >90% ee⁶⁷⁷ whereas the Rh(I)/DIOP combination carries this out in 97.3–99% ee selectivity.⁶⁷⁸ Finally, the Rh(I)/**138** system reduces β -substituted- α -arylenamides in 95–99% ee, and α -substituted acetamidoethylenes in 75.7–90% ee.⁶⁷⁴

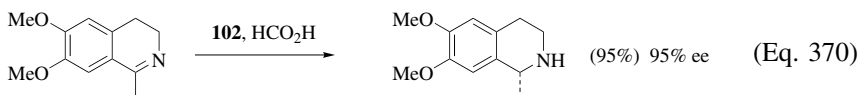
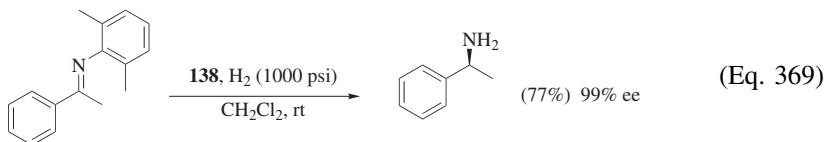


Asymmetric Hydrogenation of Imines

As an extension of the asymmetric hydrogenation of prochiral ketones to enantiomerically enriched alcohols, the reduction of imines has been a topic of interest in obtaining chiral amines of high enantiomeric purity. Several entries to enantiomerically enriched amines based on the approaches outlined above are available. These asymmetric hydrogenations have proved to be more difficult than those for prochiral ketones, but nevertheless show good promise.

Iridium(III) hydride forms complexes with DIOP, BDPP (2,4-bis(diphenylphosphino)pentane), NORPHOS, and BINAP ligands to produce amines in 11–80% ee.⁶⁷⁹ Similar modest results are obtained in the reduction of *N*-arylketimines with an iridium(III) complex with (2*S*,3*S*)-CHIRAPHOS as the chiral ligand.⁶⁸⁰ The indium complexes with chiral phosphinodihydrooxazoles catalyze the enantioselective hydrogenation of imines in supercritical carbon dioxide with up to 80% ee, but generally lower ee values are observed in

dichloromethane. The Rh(I)/chiral phosphine-catalyzed hydrogenation of imines is reported to give the chiral amines in up to 60% ee.⁶⁸¹ This work presents a crystal structure of an intermediate rhodium(diphos)imine complex. The iridium(III) complex with the diphosphine ligand **138** gives amines in up to 99% ee and in excellent yields (Eq. 369).⁶⁸² Cyclic imines undergo asymmetrical reduction via transfer hydrogenation using the catalyst EBTHI-Ti **102** (Eq. 370).⁶⁸³



The asymmetric hydrogenation of acyclic imines with the *ansa*-titanocene catalyst **102** gives the chiral amines in up to 92% ee.^{684,685} This same system applied to cyclic imines produces the chiral amines with >97% ee values.^{684,685} The mechanism of these reductions has been studied.⁶⁸⁶

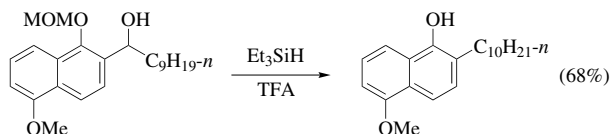
EXPERIMENTAL CONDITIONS

Normal precautions to protect laboratory workers from exposure to chemical reagents should be followed. Strong acids such as trifluoroacetic acid and trifluoromethanesulfonic acid are often used in the preparations and should be handled with extreme care. The physical properties of organosilicon hydrides are similar to those of the analogous hydrocarbons, after taking account of the differences in molecular weights. They are generally lipophilic in nature. As previously mentioned, the chemical properties of organosilicon hydrides are considerably more benign than those of many metal-based reducing agents. However, organosilicon hydrides do react with strong bases and acids to produce hydrolysis products and hydrogen gas. This reaction occurs more rapidly with bases than with acids. Also, some of the lower molecular weight organosilicon hydrides, especially the parent compound SiH₄, are pyrophoric. A few of the organosilicon hydrides, such as trimethoxysilane and triethoxysilane, are toxic and have the ability to cause corneal damage.

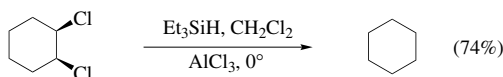
Many of the synthetically useful reactions of organosilicon hydrides are conducted in solution using solvents such as CH₂Cl₂, CHCl₃, CCl₄, MeCN, or THF. In general, it is important that anhydrous reaction conditions be used and that normal purification procedures be followed to ensure that the solvents used are pure and anhydrous.

Finally, it must be mentioned that there are advantages in synthetic methods using polymeric organosilicon hydride reagents, such as PMHS, which are both relatively inexpensive and give high molecular weight products that are reasonably easy to separate from the desired organic products.

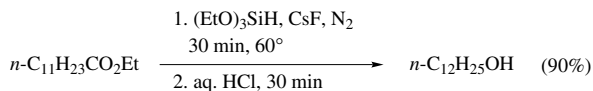
EXPERIMENTAL PROCEDURES

**2-Decyl-5-methoxy-1-naphthol [Reduction of a Secondary Benzylic Alcohol to a Methylene Group with Concomitant Loss of a MOM Protecting Group].¹⁶⁷**

To a solution of 2-(1-hydroxydecyl)-5-methoxy-1-methoxymethylenenaphthalene (0.525 g, 1.4 mmol) and Et_3SiH (1.628 g, 14 mmol) in CH_2Cl_2 (8 mL) was added TFA (2.16 mL, 28 mmol) in CH_2Cl_2 (3 mL) at room temperature and under an atmosphere of argon. The reaction mixture was stirred for 2 hours at room temperature, and then was poured into a saturated aqueous NaHCO_3 solution (20 mL) and extracted with CH_2Cl_2 (3×15 mL). The extract was washed with saturated aqueous NaHCO_3 solution (15 mL), brine (15 mL), dried with MgSO_4 , and evaporated. The crude product was purified by chromatography (SiO_2 , benzene as eluent) to afford 2-decyl-5-methoxy-1-naphthol as needles: 0.319 g (68%); mp $61\text{--}62^\circ$ (hexane); IR (CCl_4) 3600, 1600, 1505, 1254, 1055, 880 cm^{-1} ; ^1H NMR (100 MHz, CDCl_3) δ 7.60 (d, $J = 9$ Hz, 1H), 7.45 (dd, $J = 2, 8$ Hz, 1H), 7.15 (t, $J = 8$ Hz, 1H), 7.02 (d, $J = 9$ Hz, 1H), 6.56 (dd, $J = 2, 8$ Hz, 1H), 4.90 (br s, 1H), 3.94 (s, 3H), 2.68 (t, $J = 7$ Hz, 2H), 1.68 (m, 2H), 1.26 (m, 14H), 0.90 (t, $J = 8$ Hz, 3H).

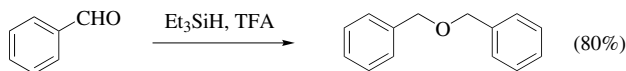
**Cyclohexane [Aluminum Chloride Catalyzed Reduction of a Dichloroalkane to a Hydrocarbon].¹⁸⁹**

After a solution of *cis*-1,2-dichlorocyclohexane (0.1582 g, 1.033 mmol) in CH_2Cl_2 (3 mL) was cooled to 0° , Et_3SiH (0.299 g, 2.57 mmol) and AlCl_3 (0.0345 g, 0.173 mmol) were added. The mixture was stirred for 30 minutes and then quenched with water (10 mL). Heptane (23.1 mg, 0.231 mmol) was added as an internal standard and the aqueous layer was separated and extracted with CH_2Cl_2 . The combined organic layer was dried (MgSO_4) and analyzed by GLC: 0.064 g (74%).

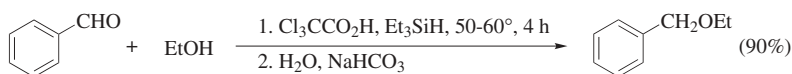
**1-Dodecanol [Fluoride-Promoted Reduction of an Ester to an Alcohol].⁸³**

A mixture of ethyl dodecanoate (2.18 g, 10.0 mmol) and triethoxysilane (3.77 g, 23.0 mmol) was added to CsF (1.52 g, 10.0 mmol) under nitrogen. The reaction was followed by IR spectroscopy. After 30 minutes at 60° , 12 N HCl (1 mL) in acetone (5 mL) was added. After 30 minutes, the mixture was extracted

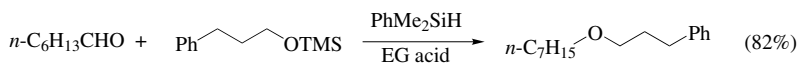
with ether (2×150 mL). The combined extracts were dried with MgSO_4 and the solvents were removed. The residue was distilled under vacuum to give 1-dodecanol: 1.8 g (90%); bp $145^\circ/15$ Torr. The GLC retention time was identical with that of an authentic sample.



Dibenzyl Ether [Brønsted Acid Promoted Reduction of an Aldehyde to a Symmetrical Ether].³¹¹ To a stirred solution of benzaldehyde (5.4 g, 0.05 mol) and TFA (11.4 g, 0.1 mol) under argon was added dropwise, with cooling, Et_3SiH (8.1 g, 0.07 mol) at a rate such that the temperature of the reaction mixture did not exceed 40° . The solution turned a crimson color that gradually disappeared. Analysis by GLC showed the complete absence of the aldehyde immediately after addition of all of the silane. The products were separated by vacuum distillation at 20 Torr, collecting the fractions up to 125° . Dibenzyl ether was obtained from the residue by freezing out: 4 g (0.02 mol, 80%); mp $3-6^\circ$; n_D^{25} 1.5608.

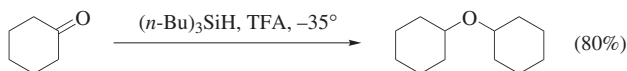


Ethyl Benzyl Ether [Brønsted Acid Promoted Reduction of an Aldehyde to an Unsymmetrical Ether].³²⁷ To a cooled mixture of benzaldehyde (4.3 g, 41 mmol) and absolute ethanol (3.7 g, 80 mmol) was added trichloroacetic acid (18.2 g, 111 mmol). Et_3SiH (6.96 g, 60 mmol) was then added dropwise with stirring while the mixture was maintained at $50-60^\circ$. After 4 hours, the reaction mixture was diluted with water, neutralized with aqueous NaHCO_3 solution, and extracted with Et_2O . The dried ether extract was distilled and the $170-190^\circ$ fraction was collected. Distillation from sodium gave ethyl benzyl ether: 4.8 g (90%); bp $187-189^\circ$.

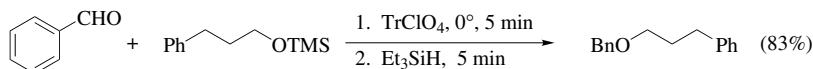


1-Heptyl 3-Phenylpropyl Ether [Electrogenerated Acid-Promoted Reduction of an Aldehyde to an Unsymmetrical Ether].³³³ A mixture of 1-heptanal (1.0 mmol), 3-phenylpropoxytrimethylsilane (1.2 mmol), tetra-*n*-butylammonium perchlorate (0.1 mmol), and lithium perchlorate (0.1 mmol) was dissolved in CH_2Cl_2 (3 mL) in an undivided cell. The mixture was electrolyzed under constant current (1.67 mA cm^{-2}) with platinum electrodes at ambient temperature. After 5 minutes, dimethylphenylsilane (1.2 mmol) was added dropwise and the electrolysis was continued (0.06 Faraday/mol). After completion of the reaction, one drop of Et_3N was added and the solution was concentrated. The residue was chromatographed on SiO_2 to give 1-heptyl 3-phenylpropyl

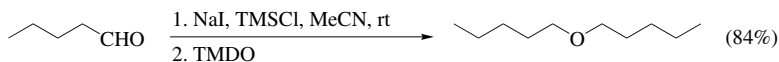
ether: 0.82 mmol (82%); bp 80–83°/1.0–2.0 Torr; IR (neat) 2955, 2925, 1605, 1110 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.22 (s, 5H), 3.37 (t, J = 6 Hz, 2H), 2.86–2.47 (m, 2H), 1.50–2.10 (m, 2H), 1.31 (br m, 10H), 0.87 (m, 3H).



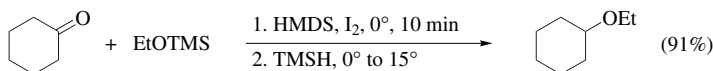
Dicyclohexyl Ether [Brønsted Acid Promoted Reduction of a Ketone to a Symmetrical Ether].³¹³ Cyclohexanone (3.92 g, 40 mmol) and tri(*n*-butyl)silane (1.78 g, 20 mmol) were placed in a round-bottomed flask. TFA (75 mmol) was added slowly over a one-hour period to the reaction mixture, which was held at -35° . After complete addition, the reaction flask was placed in a freezer at -15° for 70 hours. Direct distillation gave dicyclohexyl ether: 2.91 g (16 mmol, 80%); bp 119–121°/18 Torr.



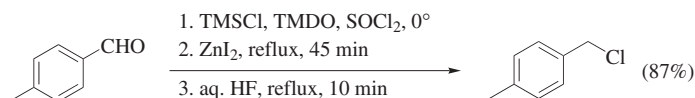
Benzyl 3-Phenylpropyl Ether [Trityl Perchlorate Catalyzed Reduction of an Aldehyde to an Unsymmetrical Ether].³²⁹ Under an argon atmosphere, a CH_2Cl_2 (2 mL) solution of benzaldehyde (53 mg, 0.5 mmol) and 3-phenylpropoxytrimethylsilane (0.5 mmol) was added to trityl perchlorate (9 mg, 0.026 mmol), and the solution was stirred for 5 minutes at 0° . A CH_2Cl_2 (1 mL) solution of Et_3SiH (59 mg, 0.5 mmol) was added and stirring was continued for another 5 minutes. Then phosphate buffer was added, and the organic materials were extracted with Et_2O and dried over MgSO_4 . After removal of the solvents under reduced pressure, isolation by TLC on SiO_2 provided 94 mg (83%) of benzyl 3-phenylpropyl ether: IR (NaCl) 1100 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.10 (s, 5H), 7.00 (s, 5H), 4.30 (s, 2H), 3.30 (t, J = 6 Hz, 2H), 2.8–2.4 (m, 2H), 2.1–1.5 (m, 2H).



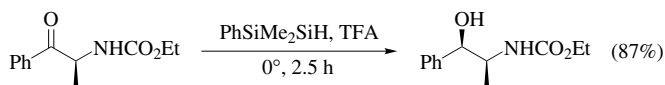
Di-*n*-pentyl Ether [TMSI-Catalyzed Reduction of an Aldehyde to a Symmetrical Ether].³¹⁴ A mixture of sodium iodide (0.15 g, 1 mmol), 1-pentanal (1.06 mL, 10 mmol), and trimethylsilyl chloride (2.0 mL, 15.4 mmol) was stirred in MeCN (5.0 mL) at room temperature for 10 minutes, after which 1,1,3,3-tetramethyldisiloxane (TMDO, 1.79 mL, 10 mmol) was added. When the exothermic reaction had ended (30 minutes), a solution of 2.5 N HF in MeOH (30 mL) was added to the reaction mixture, which was then refluxed for 5 minutes. Work-up was carried out by diluting the solution with CH_2Cl_2 (40 mL), washing with water (30 mL) and saturated aqueous NaHCO_3 solution (20 mL), drying, and evaporating the solvents. Crude di-*n*-pentyl ether was purified by distillation: 0.65 g (84%); bp 185–189°/760 Torr.



Cyclohexyl Ethyl Ether [TMSI-Catalyzed Reduction of a Ketone to an Unsymmetrical Ether].³³⁴ In a 100-mL, three-necked flask equipped with a rubber septum, thermometer, magnetic stirring bar, and nitrogen inlet were placed finely powdered iodine (0.13 g, 0.50 mmol) and hexamethyldisilane (0.079 g, 0.54 mmol) in CH_2Cl_2 (14 mL). The violet solution was stirred 10 minutes at room temperature, cooled to 0° , and a solution of cyclohexanone (1.04 g, 10 mmol) and ethoxytrimethylsilane (1.10 g, 10 mmol) in 10 mL of CH_2Cl_2 was introduced via syringe. The reaction mixture was stirred for 10 minutes at 0° , after which TMSH was added directly from a gas cylinder by means of Tygon tubing attached to a hypodermic needle inserted through the rubber septum. The gas was allowed to slowly bubble through the solution until the color changed from violet to red-gold. During this time the internal temperature rose from 0° to 15° . The cold bath was removed and stirring was continued at room temperature for 2 hours. The mixture was washed with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (4×30 mL) and water (4×30 mL), and dried over MgSO_4 . The volatiles were removed under reduced pressure on a steam bath to obtain pure cyclohexyl ethyl ether: 1.37 g (91%); bp $141\text{--}144^\circ$, ^{13}C NMR (CDCl_3) δ 76.8, 63.0, 32.6, 26.4, 24.2, 15.9.

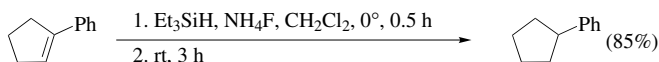


4-Methylbenzyl Chloride [Reductive Halogenation of an Aldehyde to a Benzyl Chloride].³¹⁴ A mixture of 4-methylbenzaldehyde (1.18 g, 10 mmol), chlorotrimethylsilane (2.0 mL, 15.7 mmol), 1,1,3,3-tetramethyldisiloxane (TMDO, 1.79 mL, 10 mmol), and thionyl chloride (1.0 mL, 13.7 mmol) was cooled at 0° . Then ZnI_2 (0.02 g) was added and a very exothermic reaction took place. When the spontaneous heating had ended, the mixture was heated at reflux with stirring for 45 minutes, and a 2.5 M solution of HF in MeOH (10 mL) was added. After being heated at reflux for 10 minutes, the solution was cooled to 0° , filtered, and taken up in CH_2Cl_2 (30 mL)/water (40 mL). The aqueous layer was extracted with CH_2Cl_2 (2×10 mL). The combined organic phases were dried (Na_2SO_4) and the solvents were evaporated to afford crude 4-methylbenzyl chloride, which was purified by distillation: 1.22 g, 87%; bp $190\text{--}195^\circ/760$ Torr.

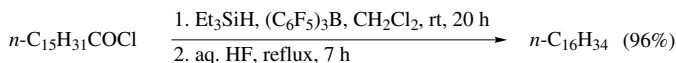


(1R,2S)-2-[(Ethoxycarbonyl)amino]-1-phenyl-1-propanol [Brønsted Acid Promoted Reduction of an α -Amino Ketone to an Erythro α -Hydroxy

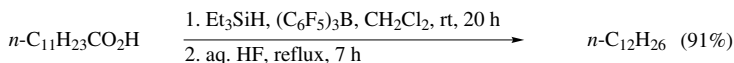
Amine].²⁷⁶ Dimethylphenylsilane (0.184 mL, 1.20 mmol) was added slowly to a TFA (1 mL) solution of (*S*)-2-[(ethoxycarbonyl)amino]-1-phenyl-1-propanone (221 mg, 1.00 mmol) at 0°, and the solution was stirred for 2.5 hours at 0°. Saturated aqueous NaHCO₃ solution (20 mL) was added, and the resulting mixture was extracted with CH₂Cl₂ (10 mL). The extract was dried over MgSO₄, filtered, and concentrated under reduced pressure to give the crude product, whose ¹H NMR spectrum showed exclusive formation (>99% selectivity) of (1*R*, 2*S*)-2-[(ethoxycarbonyl)amino]-1-phenyl-1-propanol. Purification by preparative TLC (SiO₂, AcOEt/hexane, 1/1) afforded (1*R*, 2*S*)-2-[(ethoxycarbonyl)amino]-1-phenyl-1-propanol (194 mg, 87%) as colorless crystals: mp 71°; [α]_D²⁰ − 40° (*c* 0.245, CH₂Cl₂); IR (KBr) 3350, 1694, 1552, 1273, 1043, 1028, 708 cm^{−1}; ¹H NMR (CDCl₃) δ 7.34 (s, 5H), 4.9 (br s, 1H), 4.84 (d, *J* = 3 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 4.2–3.8 (m, 1H), 2.83 (br s, 1H), 1.24 (t, *J* = 7 Hz, 3H), 0.99 (d, *J* = 7 Hz, 3H); MS (70 eV) *m/z* (relative intensity): M⁺ 223 (trace), 117 (18), 116 (66), 107 (11), 88 (21), 79 (15), 77 (14), 72 (11), 51 (5), 44 (100), 29 (23), 27 (7), 18 (5). Anal. Calcd for C₁₂H₁₇NO₃: C 64.55, H 7.67, N 6.27. Found: C 64.35, H 7.53, N 6.25.



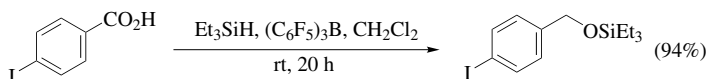
Phenylcyclopentane [Brønsted Acid Catalyzed Reduction of an Alkene to an Alkane].¹³⁵ To a stirred solution of 1-phenylcyclopentene (1.44 g, 10 mmol), NH₄F (0.48 g, 13 mmol), and Et₃SiH (1.5 g, 13 mmol) was added TFA (5.1 g, 50 mmol) at 0° over a 10-minute period. The reaction mixture was then stirred for 20 minutes at 0° and at room temperature for 3 hours. The reaction mixture was quenched with ice water and extracted with CH₂Cl₂. The organic extract was washed with 10% aqueous saturated NaHCO₃ solution, dried (CaCl₂), and concentrated. Distillation provided phenylcyclopentane: 1.22 g (85%); bp 108–111°/20 Torr.



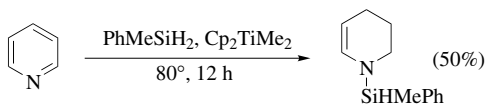
***n*-Hexadecane [Tris(pentafluorophenyl)boron-Catalyzed Reduction of an Acid Chloride to an Alkane].**²⁸² Et₃SiH (20 mmol) was added to a stirred solution of hexadecanoyl chloride (5 mmol) and tris(pentafluorophenyl)boron (5 mol%) in CH₂Cl₂. The reaction mixture was stirred for 20 hours at room temperature, quenched with Et₃N (0.25 g), filtered through Celite, and concentrated. The residue was mixed with 40% HF (5 mL) in EtOH (30 mL) and heated at reflux for 7 hours. Water (60 mL) was added, and the crude product was extracted with pentane (3 × 30 mL). The combined pentane solutions were washed with water and dried over MgSO₄. After the solvent and triethylfluorosilane were removed under vacuum, the product was purified by flash chromatography to give a 96% yield of *n*-hexadecane.



***n*-Dodecane [Tris(pentafluorophenyl)boron-Catalyzed Reduction of a Carboxylic Acid to an Alkane].**²⁸² Dodecanoic acid (5 mmol) in CH₂Cl₂ was added to a CH₂Cl₂ solution of tris(pentafluorophenyl)boron (5 mol%) and Et₃SiH (30 mmol). The reaction mixture was stirred for 20 hours at room temperature, quenched with Et₃N (0.25 g), filtered through Celite, and concentrated. The residue was mixed with 40% HF (5 mL) in EtOH (30 mL) and heated at reflux for 7 hours. Water (60 mL) was added and the crude product was extracted with pentane (3 × 30 mL). The combined pentane solutions were washed with water and dried over MgSO₄. After the solvent and triethylfluorosilane were removed under vacuum, the product was purified by flash chromatography to give a 91% yield of *n*-dodecane.

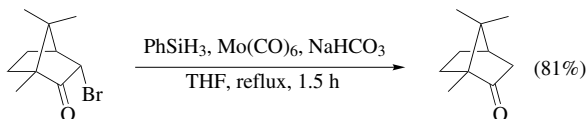


4-Iodobenzyloxytriethylsilane [Tris(pentafluorophenyl)boron-Catalyzed Reduction of a Carboxylic Acid to a Benzyl Triethylsilyl Ether].²⁸² Et₃SiH (16.5 mmol) was added to a stirred solution of 4-iodobenzoic acid (5 mmol) and tris(pentafluorophenyl)boron (5 mol%) in CH₂Cl₂. The reaction mixture was stirred for 20 hours at room temperature, quenched with Et₃N (0.25 g), filtered through Celite, and concentrated. The solvent was removed under vacuum and the product was purified by flash chromatography to give a 94% yield of 4-iodobenzyloxytriethylsilane. ¹H NMR (CDCl₃, 500 MHz) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.71 (s, 2H), 1.02, 0.68 (q, *J* = 8.0 Hz, 6H); ¹³C NMR (CDCl₃, 126 MHz) δ 140.8, 131.7, 128.3, 121.07, 64.4, 7.2, 4.9; GC-MS *m/z* (% relative intensity, ion): 300 (1, M⁺), 271 (77, M-Et), 169 (100).

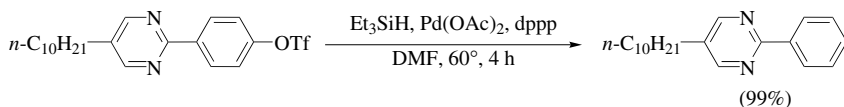


***N*-(Phenylmethylsilyl)-1,2,3,4-tetrahydropyridine [Reduction of a Pyridine].**²⁶⁴ Phenylmethylsilane (3.5 mL, 25.6 mmol) and pyridine (1.0 mL, 12.5 mmol) were added to Cp₂TiMe₂ (0.13 g, 0.7 mmol, 6 mol%). The solution color changed to dark blue, then purple, accompanied by gas evolution. The mixture was stirred for 12 hours at 80°. The ¹H-NMR spectrum showed that >95% of the pyridine had reacted to give a yield of ca. 80% of the crude product, which was distilled under vacuum to give 1.29 g (50%) of the title compound as a colorless liquid: bp 57°/0.12 Torr; ¹H NMR (300 MHz, C₆D₆) δ 7.5 and 7.2 (2m, 5H), 5.01 (q, *J* = 3.3 Hz, 1H), 4.62 (m, 1H), 2.99 (m, 2H), 2.00 (m, 2H), 1.57 (m, 2H), 0.28 (d, *J* = 3.3 Hz, 3H); ²⁹Si NMR (59.9 MHz, C₆D₆) δ -10.5;

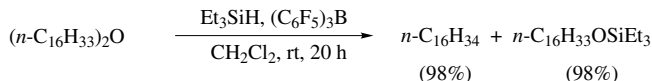
EIMS m/z (% relative intensity, ion): 203 (100, M^+), 188 (18.5, $M^+ - CH_3$), 121 (76.6, $M^+ - C_5H_8N$).



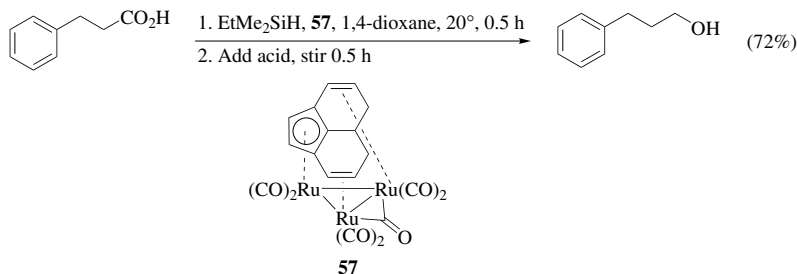
Camphor [Reduction of an α -Bromo Ketone to a Ketone].¹⁹⁷ A mixture of α -bromocamphor (2.24 g, 9.69 mmol), $Mo(CO)_6$ (0.11 g, 0.53 mmol), phenylsilane (1.30 g, 12 mmol), and $NaHCO_3$ (0.88 g, 10.5 mmol) in THF (6 mL) was heated at reflux for 1.5 hours. The mixture was cooled to room temperature, water (0.15 mL) was added, and the solvent was removed under reduced pressure. Distillation afforded camphor in 81% yield.



2-Phenyl-5-decylpyrimidine [Reduction of an Aryl Triflate to an Arene].²⁰¹ To a mixture of 2-(4-(trifluoromethanesulfonyloxy)phenyl)-5-decylpyrimidine (1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), and dppp (8 mg, 0.02 mmol) in DMF (5 mL) at 60° was added Et_3SiH (0.4 mL, 2.5 mmol). At this time the solution changed color from light brown to deep brown. Stirring was continued for 4 hours, and the reaction mixture was cooled and diluted with Et_2O . The ether phase was washed with water, and with aqueous saturated solutions of $NaHCO_3$ and $NaCl$. The ether layer was dried (Na_2SO_4) and concentrated. The crude product was purified (99% yield) by chromatography: IR (KBr) 1549, 1435, 745, 691, 654 cm^{-1} ; 1H NMR: δ 8.62 (s, 2H), 8.41 (m, 2H), 7.46 (m, 3H), 2.62 (t, $J = 7.7$ Hz, 2H), 1.8–1.4 (m, 2H), 1.27 (br s, 14H), 0.88 (t, $J = 6.2$ Hz, 3H).

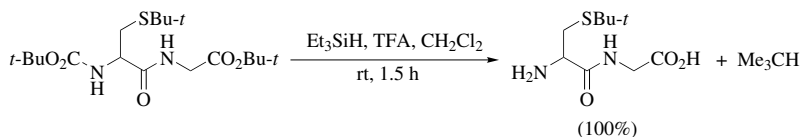


***n*-Hexadecane and 1-(Triethylsiloxy)hexadecane [Reduction of a Symmetrical Ether].**¹⁴⁵ Et_3SiH (1.1 mmol) was added to tris(pentafluorophenyl)boron (5 mol%) and bis-(*n*-hexadecyl) ether (1 mmol) in 1 mL of CH_2Cl_2 . The reaction mixture was stirred for 20 hours at room temperature and then quenched with Et_3N (0.05 mL), filtered through Celite, and concentrated. GLC analysis with an internal standard showed the presence of *n*-hexadecane (98%) and 1-(triethylsiloxy)hexadecane (98%).

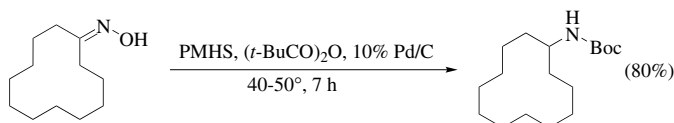


3-Phenyl-1-propanol [Reduction of a Carboxylic Acid to an Alcohol].²⁸⁰

To a solution of ruthenium catalyst **57** (616.5 mg, 25.2 μ mol) in dioxane (0.45 mL) was added dimethylethylsilane (0.84 mL, 6.3 mmol). After the mixture had been stirred for 30 minutes at room temperature, hydrocinnamic acid (380 mg, 2.55 mmol) was added, and the stirring was continued for 30 minutes. Vigorous gas evolution occurred. The reaction was quenched with aqueous HCl, and the mixture was extracted with Et₂O. The organic phase was washed with aqueous saturated NaHCO₃ and aqueous saturated NaCl solutions, and then dried with MgSO₄. The solvent was removed under vacuum and the product was purified by chromatography (EtOAc/hexane 1/9) to give 3-phenylpropyl alcohol: 248 mg, 72%.

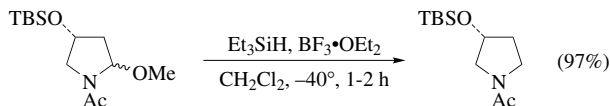


Cys(SBu-*t*)Gly [Reductive Deprotection of Boc and *tert*-Butyl Ester Groups in the Presence of a *tert*-Butyl Sulfide].³⁰⁷ Boc-Cys(SBu-*t*)Gly-OBu-*t* (1 mmol) was stirred with TFA (13 mmol), CH₂Cl₂ (32 mmol), and Et₃SiH (2.5 mmol) at room temperature for 1.5 hours. After solvent removal, the residue was triturated with Et₂O and the precipitated product was removed by filtration, washed with Et₂O, and dried: 100%.

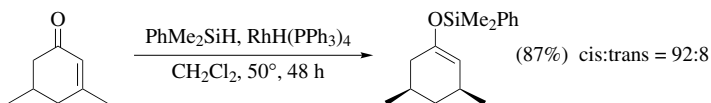


N-Boc-cyclododecylamine [Reductive Boc-protection of an Oxime].⁵⁴⁹

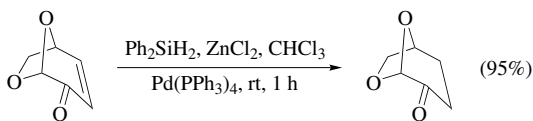
To a stirred solution of cyclododecanone oxime (1 mmol) in EtOH (10 mL) were added PMHS (180 mg, 3.0 mmol), di-*tert*-butyl dicarbonate (240 mg, 1.1 mmol), and 10% Pd/C (10 mg). The reaction mixture was stirred at 40–50° for 7 hours, after which time it was filtered and the filtrate concentrated under vacuum. The crude product was purified by column chromatography to give *N*-Boc-cyclododecylamine: 80%.



(3*R*)-*N*-Acetyl-3-(*tert*-butyldimethylsiloxy)pyrrolidine [Reduction of an Aminoal to an Amine].⁵²¹ A solution of *N*-acetyl-2-methoxy-4-*tert*-butyldimethylsiloxy)pyrrolidine (2 mmol) and Et_3SiH (4 mmol) in dry CH_2Cl_2 (3 mL) was treated with $\text{BF}_3 \cdot \text{OEt}_2$ (4 mmol) at -40° . The reaction was monitored by TLC (1–2 hours). The mixture was diluted with CHCl_3 and washed with aqueous saturated NaHCO_3 and aqueous saturated NaCl solution. The organic layer was dried (MgSO_4) and evaporated under reduced pressure. Purification of the residue by chromatography on SiO_2 (hexane/ EtOAc 10:1) gave the title compound as a colorless syrup: 97%; $[\alpha]^{24.5}_{\text{D}} -23.4^\circ$ (c 1.22, CHCl_3); IR (film) $3350, 1650 \text{ cm}^{-1}$; ^1H NMR (CDCl_3) δ 4.58–4.25 (m, 1H), 3.80–3.10 (m, 4H), 2.10–1.60 (m, 2H), 1.98, 1.95 (2s, 3H), 0.80 (s, 9H), 0.01 (s, 6H); MS m/z : 228 ($\text{M}^+ - \text{CH}_3$); Anal. Calcd for $\text{C}_{12}\text{H}_{25}\text{NO}_2\text{Si}$: C 59.21; H 10.35; N 5.75; Si 11.54. Found: C 58.85; H 10.38; N 5.80; Si 11.18.

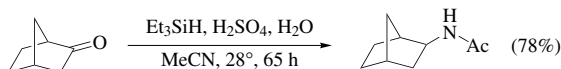


3,5-Dimethyl-1-cyclohexen-1-yl Dimethylphenylsilyl Ether [Reductive 1,4-Hydrosilylation of an Enone].³⁷⁴ 3,5-Dimethyl-2-cyclohexen-1-one (0.124 g, 1.0 mmol) and $\text{RhH}(\text{PPh}_3)_4$ (6 mg, 0.0052 mmol) were treated with PhMe_2SiH (0.177 g, 1.3 mmol) at 50° for 48 hours. After hexane (1 mL) was added, the reaction mixture was filtered and concentrated under vacuum. The crude product was purified by Kugelrohr distillation ($90^\circ/1$ Torr) to give a colorless liquid: 225 mg, 87%; IR 2952, 2918, 2913, 2902, 2870, 1666, 1428, 1369, 1253, 1197, 1182, 1121, 1079, 826, 787, 699 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.58 (m, 2H), 7.37 (m, 3H), 4.66 (s, 1H), (s, 1H), 2.21 (br s, 1H), 1.93 (m, 1H), 1.63 (m, 4H), 0.90 (d, $J = 7.9 \text{ Hz}$, 3H), 0.86 (d, $J = 7.0 \text{ Hz}$, 3H), 0.43 (s, 6H); ^{13}C NMR δ 149.7, 138.0, 133.4, 129.5, 127.7, 111.3, 40.8, 38.4, 30.9, 29.6, 22.6, 22.0, -0.9 , -1.0 ; EIMS m/z : M^+ calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$, 260.1596; found 260.1584. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: C 73.80; H 9.30; found: C 73.78; H 9.25.

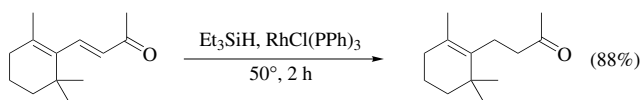


6,8-Dioxabicyclo[3.2.1]octan-4-one [1,2-Reduction of an Enone in the Presence of an Acetal].⁴³⁶ 6,8-Dioxabicyclo[3.2.1]oct-2-ene-4-one (19 mg, 0.15 mmol) was dissolved in 3 mL of CHCl_3 along with Ph_2SiH_2 (55 mg,

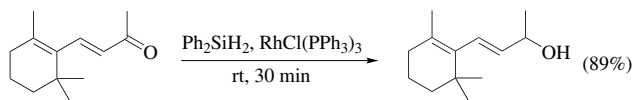
0.30 mmol) and ZnCl_2 (20 mg, 0.15 mmol). $\text{Pd}(\text{PPh}_3)_4$ (17 mg, 0.015 mmol) was added and the mixture was stirred at room temperature until the reaction was complete as determined by GLC. The reaction mixture was filtered through a short SiO_2 column and purified by Kugelrohr distillation to give 18 mg (95%) of 6,8-dioxabicyclo[3.2.1]octan-4-one, having physical properties identical with literature values.



***N*-(*exo*-2-Norbornyl)acetamide [Reductive Amidation of a Ketone].**³¹³ To an acetonitrile (15 mL) solution of norcamphor (6.6 g, 60 mmol) and triethylsilane (7.7 g, 66 mmol) was added water (3.0 mL) followed by 9.0 mL of concentrated H_2SO_4 (9.0 mL) at ice-bath temperature. The heterogeneous reaction mixture was stirred rapidly at room temperature for 65 hours. The mixture was then quenched by addition of 50% aqueous NaOH solution (30 mL) and the aqueous solution was extracted with CH_2Cl_2 (3×50 mL). The combined extracts were passed through anhydrous MgSO_4 and the CH_2Cl_2 was removed under reduced pressure. The residue was washed three times with pentane to remove hexamethyldisiloxane and other soluble reaction products. The crude product was crystallized from Et_2O to give *N*-(*exo*-2-norbornyl)acetamide (6.5 g, 78%) whose ^1H -NMR spectrum and melting point were in accord with literature values.

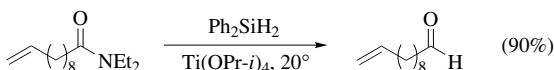


Dihydro- β -ionone [1,4-Reduction of an α,β -Unsaturated Ketone].⁴³⁵ A mixture of β -ionone (1.91 g, 10 mmol), Et_3SiH (1.27 g, 11 mmol), and $\text{RhCl}(\text{PPh}_3)_3$ (9 mg, 0.01 mmol) was stirred at 50° for 2 hours under nitrogen. The NMR spectrum of the reaction mixture showed the exclusive formation of the 1,4-addition (silyl enol ether) product: ^1H NMR (CCl_4) δ 5.23 (m, 1H), 4.28 (t, $J = 7$ Hz, 1H), 2.25–1.75 (m, 4H), 1.72 (br s, 3H), 1.63 (br s, 3H), 1.75–1.20 (m, 3H), 0.4–1.20 (m, 21H). The silyl enol ether was readily desilylated by treatment with K_2CO_3 (10 mg)/MeOH (10 mL) with stirring for 1 hour at room temperature. After solvent removal, the crude product was distilled under reduced pressure to give dihydro- β -ionone: 1.70 g, 88.1% bp $88^\circ/2.5$ Torr.

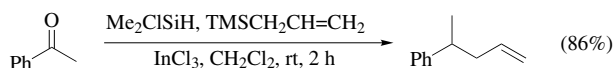


β -Ionol [1,2-Reduction of an α,β -Unsaturated Ketone].⁴³⁵ A mixture of β -ionone (1.93 g, 10 mmol), Ph_2SiH_2 (2.02 g, 11 mmol), and $\text{RhCl}(\text{PPh}_3)_3$ (9 mg, 0.01 mmol) was stirred at room temperature under nitrogen. An

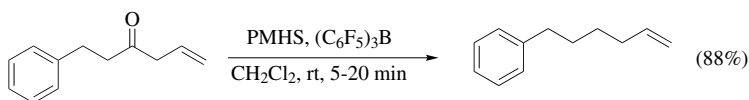
exothermic reaction took place and the reaction was complete in 30 minutes. The NMR spectrum of the reaction mixture indicated the 1,2-reduction (silyl ether) product was formed exclusively: ^1H NMR (CCl_4) δ 7.80-7.10 (m, 10H), 5.55-5.18 (m, 3H), 5.40 (s, 1H), 4.39 (m, 1H), 2.30-1.00 (m, 5H), 1.53 (m, 3H), 1.27 (d, $J = 6$ Hz, 3H), 1.0 (m, 5H), 0.86 (s, 3H), 0.77 (s, 3H). To the reaction mixture was added *n*-hexane (50 mL), and the precipitated catalyst was removed by filtration. Then MeOH (10 mL) and K_2CO_3 (10 mg) were added to the filtrate. Methanolysis was complete within 1 hour at room temperature. The ratio of dihydro- β -ionone/ β -ionol was 0 : 100 based on GLC and NMR analyses. After solvent evaporation, the residue was distilled to give β -ionol: 1.74 g, 89%; bp $99^\circ/2$ Torr.



Undec-10-enal [Reduction of an Amide to an Aldehyde].⁴³³ To a dry flask containing neat *N,N*-diethylundec-10-enamide (0.155 mL, 0.65 mmol) under argon was added Ph_2SiH_2 (0.135 mL, 0.72 mmol) and $\text{Ti(OPr-}i\text{)}_4$ (0.196 mL, 0.65 mmol). Initial effervescence was observed [CAUTION!] and the reaction mixture was stirred at room temperature until TLC analysis showed complete consumption of the starting material (ca. 5 hours). The mixture was diluted with THF (20 mL), treated with 1 M HCl (10 mL), stirred for 1 hour, and poured onto Et_2O (80 mL). The organic layer was washed with 1 M HCl (3×10 mL), saturated aqueous NaHCO_3 solution (2×10 mL), and saturated aqueous NaCl solution (10 mL), and then dried (MgSO_4) and concentrated under vacuum. Flash column chromatography on SiO_2 (hexane: Et_2O 15 : 85) afforded undecenal (99 mg, 90%).

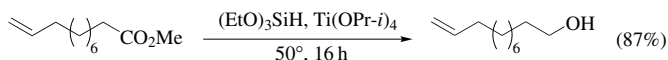


4-Phenylpent-1-ene [Reductive Allylation of an Aryl Ketone].⁴²⁷ Acetophenone (2.0 mmol) was added to a mixture of InCl_3 (0.1 mmol), ClMe_2SiH (2.2 mmol), and allyltrimethylsilane (2.2 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was stirred for 2 hours, quenched with water (20 mL), and extracted with Et_2O (3×20 mL). After the organic layer was dried (MgSO_4) and concentrated under vacuum, the residue was purified by chromatography (hexane) on SiO_2 to give 4-phenylpent-1-ene (86%).

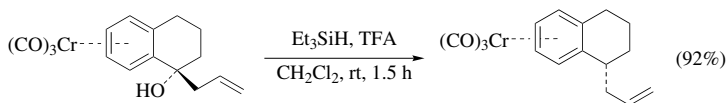


6-Phenylhex-1-ene [Reduction of an Aliphatic Ketone Function to a Methylene Function].³⁵⁴ To a solution of 6-phenylhex-1-ene-4-one (1 mmol) in

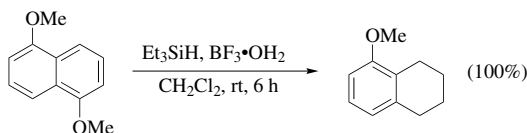
dry CH_2Cl_2 (5 mL) and tris(pentafluorophenyl)boron (5 mol%) was slowly added PMHS (3 mmol) at room temperature. After 20 minutes, a vigorous effervescence was observed. The solvent was evaporated and the reaction mixture was dissolved in hexane and then filtered through a SiO_2 pad using hexane. Evaporation of the volatiles afforded the 6-phenylhex-1-ene (88%) in pure form.



10-Undecen-1-ol [Reduction of an Ester to an Alcohol].²⁹¹ Triethoxysilane (1.7 mL, 9 mmol) and methyl 10-undecenoate (594 mg, 3 mmol) were added to a test tube. $\text{Ti}(\text{OPr-}i)_4$ (45 μL , 0.15 mmol) was added, and the test tube was fitted with a drying tube packed with Drierite to exclude excess moisture. The contents of the vessel were then stirred while being heated in an oil bath at 50° for 16 hours. The reaction mixture was washed into a 100-mL round-bottomed flask with THF (10 mL). Then 1 N NaOH (20 mL) was added slowly with stirring. NOTE: CAUTION: vigorous bubbling was observed. After 4 hours, the mixture was added to Et_2O (50 mL) and water (50 mL). After shaking, the layers were separated, and the aqueous layer was extracted with an additional 50 mL of Et_2O . The combined organic extracts were washed with 1 M HCl (2×50 mL), dried (MgSO_4), filtered, and concentrated under vacuum to afford 10-undecen-1-ol as a clear oil: 443 mg, 87%. The product was >95% pure as determined by GLC and ^1H NMR analyses.

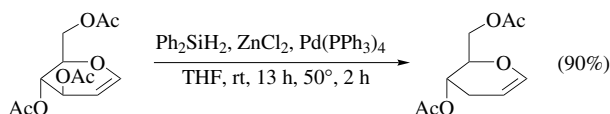


Tricarbonyl(1-endo-allyltetralin)chromium [Stereoselective Reduction of an Alcohol to a Hydrocarbon].¹⁸² A solution of tricarbonyl(1-*exo*-allyl-1-*endo*-tetralol)chromium (150 mg, 0.46 mmol), Et_3SiH (0.22 mL, 1.4 mmol), and CH_2Cl_2 (1 mL) was stirred at room temperature for 1.5 hours under nitrogen. The mixture was poured into water (10 mL) and extracted with Et_2O (2×10 mL). Evaporation of the organic layer under reduced pressure and purification by silica gel chromatography on SiO_2 (1 : 8 Et_2O /petroleum ether) afforded tricarbonyl(1-*endo*-allyltetralin)chromium as yellow crystals: 131 mg, 92%; mp $88\text{--}89^\circ$; IR (CHCl_3) $1960, 1880, 1635\text{ cm}^{-1}$; ^1H NMR (CDCl_3) δ 6.15–4.80 (m, 7H), 2.95–2.10 (m, 5H), 2.05–1.35 (m, 4H).

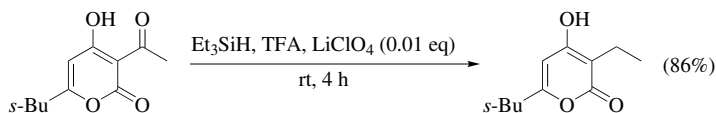


5-Methoxytetralin [Partial Reduction of a Substituted Naphthalene to a Tetralin].²⁶² 1,5-Dimethoxynaphthalene (300 mg, 1.0 mmol) dissolved in

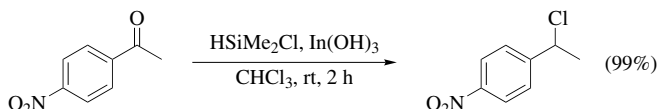
CH_2Cl_2 (3–4 mL) was added dropwise to a flask containing $\text{BF}_3 \cdot \text{OH}_2$ (1.1 g, 13 mmol) at 0° . After the addition was completed, the mixture was stirred for 10–15 minutes and allowed to warm to room temperature, and Et_3SiH (742 mg, 6.4 mmol) was added dropwise. The reaction mixture was stirred at room temperature for an additional 5–6 hours, neutralized with cold saturated aqueous Na_2CO_3 solution, and extracted with CH_2Cl_2 (3×15 mL). The combined organic extracts were washed with water (2×10 mL), dried (MgSO_4), and evaporated to leave ca. 270 mg of brownish oil, which according to NMR and GC analyses contained ca. 90% of 5-methoxytetralin. Purification of the crude product was accomplished by column chromatography on SiO_2 ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$).



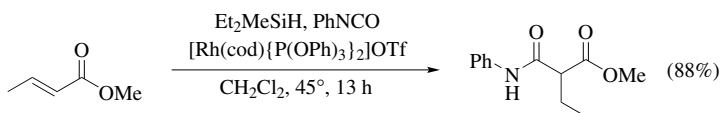
1,2,3-Trideoxy-D-ribo-hex-1-enopyranose Diacetate [Reduction of an Allyl Ester].¹⁹⁶ To a THF (10 mL) solution containing tri-*O*-acetylglucal (349 mg, 1.28 mmol), diphenylsilane (489 mg, 403 mmol), and ZnCl_2 (541 mg, 4.0 mmol) was added $\text{Pd}(\text{PPh}_3)_4$ (70 mg, 0.06 mmol, 12 mol%). The solution was stirred at room temperature for 13 hours, then at 50° for 2 hours, and then mixed with Et_2O and washed several times with water. The ether layer was dried over Na_2SO_4 and the solvent was evaporated. The yield of 1,2,3-trideoxy-D-ribo-hex-1-enopyranose diacetate was 90% as determined by NMR using bibenzyl as an internal standard. The product was partially decomposed upon chromatographic purification over SiO_2 , yielding 120 mg (53%).



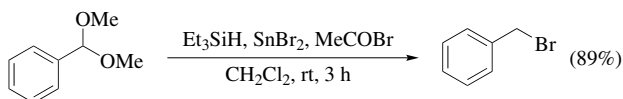
6-(2-Butyl)-4-hydroxy-3-ethyl-2-pyrone (Germicidin) [Reduction of a Ketone Carbonyl to a Methylene Group in a Multifunctional Compound].⁴²³ A TFA (15 mL) solution containing 3-acetyl-6-(2-butyl)-4-hydroxy-2-pyrone (2 mmol), Et_3SiH (1.29 mL, 8.0 mmol), and LiClO_4 (2 mg, 0.02 mmol) was stirred at room temperature for about four hours while being monitored by TLC. The solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel (CHCl_3 eluent) to yield racemic 6-(2-butyl)-4-hydroxy-3-ethyl-2-pyrone: 337 mg, 86%; mp $95\text{--}97^\circ$ (Et_2O /hexane); IR (KBr) 1160, 1285, 1430, 1595, 1680, 2885, 2945, 2980 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.22 (s, 1H), 2.48 (q, $J = 7.4$ Hz, 2H) and (m, 1H), 1.75–1.24 (m, 2H), 1.20 (d, $J = 6.7$ Hz, 3H), 1.11 (t, $J = 7.5$ Hz, 3H), 0.89 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 69.6, 168.8, 168.0, 105.0, 100.9, 39.8, 27.5, 17.7, 16.4, 12.4, 11.6.



1-(1-Chloroethyl)-4-nitrobenzene [Deoxygenative Chlorination of a Ketone].³³¹ To a mixture of In(OH)_3 (0.1 mmol) and *p*-nitroacetophenone (2.0 mmol) in CHCl_3 (4.0 mL) was added ClSiMe_2H (2.4 mmol) under nitrogen. The reaction mixture was stirred for 2 hours at room temperature, and then was poured into EtOAc (50 mL) and washed with saturated aqueous NaHCO_3 solution (50 mL). The organic layer was dried over MgSO_4 and concentrated under vacuum to yield 99% of 1-(1-chloroethyl)-4-nitrobenzene. The physical and spectral data of the product were in excellent accord with known values.

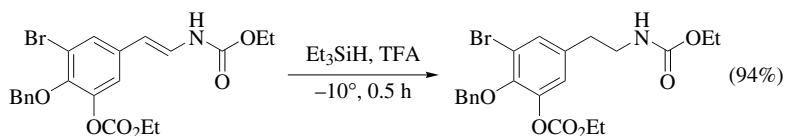


Methyl 2-(Phenylcarbamoyl)butanoate [Hydrocarbamoylation of an α,β -Unsaturated Ester].⁴⁷⁵ To a solution of $[\text{Rh(cod)\{P(OPh)_3\}_2}\text{OTf}]$ (9.9 mg, 0.01 mmol) in CH_2Cl_2 (4 mL) was added a mixture of phenyl isocyanate (121 mg, 1.0 mmol), methyl crotonate (210 mg, 2.1 mmol), and Et_2MeSiH (205 mg, 2.0 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was heated at reflux for 13 hours under a nitrogen atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on SiO_2 (4:1 hexane/ EtOAc) to afford methyl 2-(phenylcarbamoyl)butanoate: 194 mg, 88%; mp $76.0\text{--}77.0^\circ$ (hexane/ EtOAc); IR (CCl_4) 3371, 1722, 1689 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.74 (br s, 1H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.30 (dd, $J = 8.4$ and 7.5 Hz, 2H), 7.10 (t, $J = 7.5$ Hz, 1H), 3.76 (s, 3H), 3.32 (t, $J = 7.3$ Hz, 1H), 2.03 (dq, $J = 7.4$ and 7.3 Hz, 2H), 0.99 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 172.7, 166.3, 137.4, 128.8, 124.3, 119.9, 54.9, 52.5, 24.9, 11.8. Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_3$: C 65.14; H 6.83; N 6.33. Found: C 65.30; H 6.57; N 6.28.

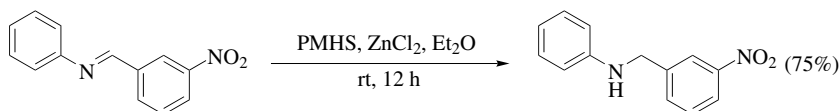


Benzyl Bromide [Reductive Bromination of an Acetal].⁵⁰⁶ To a suspension of tin(II) bromide (5.1 mg, 0.02 mmol) and benzaldehyde dimethyl acetal (54.8 mg, 0.36 mmol) in CH_2Cl_2 (2.5 mL) were added successively Et_3SiH (65.0 mg, 0.56 mmol) and acetyl bromide (96.8 mg, 0.79 mmol) in CH_2Cl_2 (1 mL) at room temperature under an argon atmosphere. The mixture was stirred for 3 hours at room temperature and quenched with a phosphate buffer (pH 7).

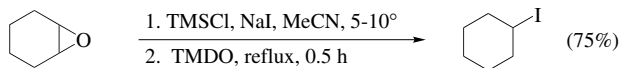
The organic materials were extracted with CH_2Cl_2 and the extract was dried over Na_2SO_4 . Benzyl bromide (54.7 mg, 89%) was isolated by TLC on SiO_2 .



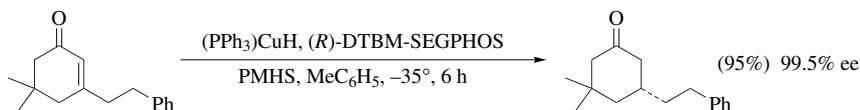
2-(Benzyloxy)-3-bromo-5-[(2-ethoxycarbonyl)ethyl]phenyl Ethyl Carbamate [Reduction of an Enamide to an Amide].⁵³⁵ A mixture of Et_3SiH (170 μL , 1.07 mmol) and (*E*)-2-(benzyloxy)-3-bromo-5-(2-ethoxycarbonyl)vinylphenyl ethyl carbamate (32 mg, 0.69 mmol) was cooled to -10° in an ice-salt bath under nitrogen, and treated with pre-cooled TFA (1.0 mL) in one portion. The two-phase mixture was *rapidly* stirred at -10° for 0.5 hour, poured into ice-cold saturated aqueous NaHCO_3 solution, and worked up by extraction with CH_2Cl_2 . The extracts were dried (Na_2SO_4) and concentrated to give essentially pure title product: 30 mg, 94%; ^1H NMR (CDCl_3) δ 7.5–7.3 (m, 5H), 7.29 (d, $J = 2.0$ Hz, 1H), 6.96 (d, $J = 2.0$ Hz, 1H), 4.99 (s, 2H), 4.74 (br t, $J = 5.6$ Hz, 1H), 4.21 (q, $J = 7.2$ Hz, 2H), 4.10 (q, $J = 7.2$ Hz, 2H), 3.38 (dt, $J = 5.6$ and 6.8 Hz, 2H), 2.74 (t, $J = 6.8$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.22 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 156.5, 152.9, 146.8, 145.1, 136.6, 136.4, 131.1, 128.4, 128.3, 128.2, 122.6, 118.1, 75.5, 65.2, 60.8, 41.7, 35.2, 14.6, 14.1; HRMS (CI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{25}\text{BrNO}_6$, 466.0865; found, 466.0864.



3-Nitrobenzylamine [Reduction of an Imine to an Amine].⁵³⁹ To PMHS (300 mg) in a 25-mL flask fitted with a septum inlet and magnetic stirring bar was added freshly fused ZnCl_2 (270 mg, 5 mmol) in dry Et_2O (5 mL) under a nitrogen atmosphere. After 10 minutes, *N*-phenyl-3-nitrophenylmethanimine (225 mg, 1 mmol) was added, and the reaction mixture was stirred at room temperature for 12 hours and extracted with 1 M HCl (2×15 mL). The aqueous layer was washed with CH_2Cl_2 (15 mL) to remove non-amine impurities. The purified aqueous layer was made basic (pH ~ 10) with 1 N NaOH and extracted with EtOAc (3×15 mL). The combined organic layers were washed with water (15 mL) and brine (15 mL), and dried (Na_2SO_4). The volatiles were removed and the residue was purified by column chromatography to yield 170 mg (75%) of the title product: ^1H NMR (CDCl_3) δ 7.20 (d, $J = 7.5$ Hz, 2H), 7.70–6.50 (m, 7H), 3.50 (s, 2H); MS m/z : M^+ 228, 136, 106, 91, 77.



Cyclohexyl Iodide [Iodoreduction of an Oxirane to an Iodoalkane].³⁵⁷ A mixture of cyclohexene oxide (1.01 mL, 10 mmol), NaI (2.00 g, 13.3 mmol), and TMSCl (1.92 mL, 15 mmol) in anhydrous MeCN (10 mL) was stirred at 5–10° for 2–3 minutes. Then TMDO (1.79 mL, 10 mmol) was added and the mixture was heated at reflux for 0.5 hour. The remaining siloxane products were destroyed by adding 45% aqueous HF (2.0 mL) and heating at reflux for 5 minutes. The reaction mixture was taken up in CH₂Cl₂ (30 mL), and the organic layer was washed with water (20 mL), 1 N NaHSO₃ (10 mL), and water (20 mL) again. Drying (Na₂SO₄) and evaporation of the solvents afforded crude cyclohexyl iodide, which was purified by Kugelrohr distillation to give pure product, 1.58 g (75%); bp 180–183°; ¹H NMR (CCl₄) δ 4.14 (m, 1H), 1.92 (m, 4H), 1.41 (m, 6H).



(*R*)-3,3-Dimethyl-5-(2-phenylethyl)cyclohexanone [Asymmetric 1,4-Reduction of an Enone].⁵⁹⁷ To a 5-mL round-bottomed flask, flame-dried and purged with argon, was added CuHPPH₃ (2.3 mg, 7.0 μ mol) and (*R*)-DTBM-SEGPHOS (1.9 mg, 1.6 μ mol). Toluene (0.60 mL) was added and the solution was cooled to –35°. After PMHS (215 μ L, 3.3 mmol) was introduced by syringe, 3-(2-phenylethyl)-5,5-dimethylcyclohexenone (192 mg, 0.84 mmol) was added. The mixture was stirred at –35° for 12 hours until the reaction was complete as determined by TLC (20% Et₂O/ligroin) and was then quenched by pouring into 3 N NaOH. Ether and water were added, and the mixture was stirred for 2 hours at room temperature. The aqueous layer was extracted with Et₂O (2 x), and the combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (10% Et₂O/ligroin) to afford the title ketone as a clear oil: 185 mg (95%), chiral GC (ketal from (*R,R*)-2,3-butanediol, Chiraldex B-DM 140) showed 99.5% ee. ¹H NMR (CDCl₃, 400 MHz) δ 7.31–7.17 (m, 5H), 2.64 (t, *J* = 8.2 Hz, 2H), 2.44 (ddd, *J* = 9.2, 2.0, 2.0 Hz, 1H), 2.21 (d, *J* = 13.2 Hz, 1H), 2.10 (ddd, *J* = 13.2, 2.2, 2.2 Hz, 1H), 1.35 (t, *J* = 12.4 Hz, 1H), 1.09 (s, 3H), 0.88 (s, 3H), 1.99–1.91 (m, 2H), 1.73–1.62 (m, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 25.3, 32.3, 33.2, 34.6, 35.4, 39.3, 45.3, 47.6, 54.7, 126.0, 128.4, 128.6, 142.2, 212.0; HRMS calcd for C₁₆H₂₂O 230.1671; found 230.1663.

TABULAR SURVEY

A thorough coverage of the literature through 2004 has been carried out based on the search of certain silanes. A small number of additional pertinent articles,

particularly regarding the asymmetric silane reductions that were published later, are included.

Tables are organized by the functional group classes undergoing change in the substrates. Table entries are ordered by increasing carbon count of the starting substrate. Protecting groups are included in the carbon count. Unspecified yields are denoted by (—).

The following abbreviations are used in the tables:

10-C-6	10-crown-6
18-C-6	18-crown-6
Ac	acetyl
acac	acetylacetone
ACHN	1,1'-azobis(cyclohexylnitrile)
Ad	adamantyl
AIBN	azobis(isobutyronitrile)
An	anthracenyl
BARF	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
BDE	bond dissociation energy
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINOL	1,1'-bi-2-naphthol
BIPHEMP	2,2'-bis(diphenylphosphino)-6,6'-dimethyl-1,1'-biphenyl
BIPHEP	2,2'-bis(diphenylphosphino)-1,1'-biphenyl
bipy	bipyridyl
Bipymox	6,6'-bis(oxazoliny)-2,2'-bipyridine
Bmpp	benzylmethylphenylphosphine
Bn	benzyl
Boc	<i>tert</i> -butyloxycarbonyl
BOM	benzyloxymethyl
BOX	bis(oxazolino)
BPPFA	1',2-bis[diphenylphosphinoferrocenyl]ethyl dimethylamine
BSA	bis(trimethylsilyl)acetamide
BTAF	benzyltrimethylammonium fluoride
Bz	benzoyl
Cbz	carbobenzyloxy
cod	1,5-cyclooctadiene
coe	cyclooctene
cot	cyclooctatetraene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
CSA	camphorsulfonic acid
DAST	(diethylamino)sulfur trifluoride
dba	dibenzylidene acetone
DBATO	dibutylacetoxystin oxide
dbpp	di-(<i>tert</i> -butylphenyl)phosphite
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene

DCE	1,2-dichloroethane
de	diastereomeric excess
dea	diethanolamine
dee	diethoxyethane
DIBALH	diisobutylaluminum hydride
DIPOF	[2-(4,5-diphenyl-4,5-dihydro-1,3-oxazolin-2-yl)-ferrocenyl]diphenylphosphine
DIOP	(2 <i>S</i> ,3 <i>S</i>)- <i>O</i> -isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane
diphos	1,2-bis(diphenylphosphino)ethane (see dppe)
DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMI	1,3-dimethyl-2-imidazolidinone
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2-(1 <i>H</i>)-pyrimidinone
DMSO	dimethyl sulfoxide
DMTS	dimethylthexylsilyl
dpm	2,2,6,6-tetramethylheptane-3,5-dionate ("dipivaloylmethanato")
dppb	1,4-bis(diphenylphosphino)butane
dppbz	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphino)ethane
dppf	bis(diphenylphosphino)ferrocene
dppfc	diphenylphosphinoferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
dr	diastereomeric ratio
ds	diastereoselectivity
dma	dimethylacetamide
ebpe	<i>N,N'</i> -ethylenebis(1-phenylethylamine)
EBTHI	ethylenebis(η^5 -tetrahydroindenyl)titanium
ee	enantiomeric excess
EE	ethoxyethyl
EG	electrogenerated
EH	2-ethylhexanoate
er	enantiomeric ratio
Fc	ferrocene
Fmoc	fluorenylmethoxycarbonyl
HAp	hydroxyapatite
HMDS	hexamethyldisilazane
H-MOP	2-diphenylphosphino-1,1'-binaphthyl
HMPA/HMPT	hexamethylphosphoric triamide
KU-1	phenol-formaldehyde sulfocationite
LAH	lithium aluminum hydride
Me-DuPHOS	1,2-bis-(2,5-dimethylphospholano)benzene
MEM	methoxyethoxymethyl

MOM	methoxymethyl
Ms	methanesulfonyl
mont	montmorillonite
MPM	methoxyphenylmethyl
NBD	norbornadiene
Nf	nonaflate
nmdpp	(<i>S</i>)-neomenthyldiphenylphosphine
NMP	<i>N</i> -methylpyrrolidone
NORPHOS	(-)-(<i>R,R</i>)-2- <i>exo</i> -3- <i>endo</i> -bis(diphenylphosphino)- bicyclo[2.2.1]hept-5-ene
Np	naphthyl
NR	no reaction
Ns	4-nitrobenzenesulfonate
<i>o</i> -dppb	1,2-bis(diphenylphosphino)benzene
OTFA	trifluoroacetate
PE	phosphatidylethanolamine
Piv	pivaloyl
PEHS	polyethylhydrogensiloxane
PMB	<i>p</i> -methoxybenzyl
PMHS	polymethylhydrogensiloxane
PNB	<i>p</i> -nitrobenzoate
PPA	polyphosphoric acid
PPFA	[<i>N,N</i> -dimethyl-1[2-(diphenylphosphino)- ferrocenyl]ethylamine
ppf	2-[diphenylphosphinoferrocenyl]ethyl dimethylamine
PPHF	pyridinium poly(hydrogen fluoride)
PPTS	pyridinium <i>p</i> -toluenesulfonate
PTC	phase-transfer catalysis
P(tm-tp) ₃	tris(2,2'',6,6''-tetramethyl- <i>m</i> -terphenyl-5'-yl)phosphane
P(tp) ₃	tris(<i>m</i> -terphenyl-5'-yl)phosphane
<i>p</i> -Tol-BINAP	2,2'-bis(<i>p</i> -tolylphosphino)-1,1'-binaphthyl
PTSA	<i>p</i> -toluenesulfonic acid
pybox	pyridinebis(oxazoline)
pymox	pyridinemono(oxazoline)
rt	room temperature
SEGPPOS	(4,4'-bi-1,3-benzodioxole)-5,5'-diylbis(diarylphosphine)
TADDOL	$\alpha,\alpha',\alpha',\alpha'$ -tetraaryl-1,2-dioxolane-4,5-dimethanol
TASF	tris(diethylamino)sulfonium difluorotrimethylsilicate
TBAF	tetra- <i>n</i> -butylammonium fluoride
TBAT	tetrabutylammonium triphenyldifluorosilicate
TBDPS	<i>tert</i> -butyldiphenylsilyl
TBS	<i>tert</i> -butyldimethylsilyl
TEA	triethylamine
TEAF	tetraethylammonium fluoride
TES	triethylsilyl

Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
TFPB	tetrakis-3,5-bis(trifluoromethylphenyl)borate
THEATi(OPr- <i>i</i>)	[tris(hydroxyethyl)amino]titanium(IV)isopropoxide
THF	tetrahydrofuran
THP	tetrahydropyran
TIPS	triisopropylsilyl
TMDO	1,1,3,3-tetramethyldisiloxane
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMS	trimethylsilyl
TMSBr	trimethylsilyl bromide
TMSCl	trimethylsilyl chloride
TMSI	trimethylsilyl iodide
Tol	tolyl
Tr	triphenylmethyl
TRAP	2,2'-bis[(dialkylphosphino)methyl]-1,1'-biferrocene
TRISPHOS	2,2',2''-tris(2,4,8,10)-tetra- <i>tert</i> -butyldibenzo[<i>d,f</i>]- [1,3,2]dioxaphosphepin-6-yl-6-oxy)tri-2-propylamine
Trityl	triphenylmethyl
Ts	<i>p</i> -toluenesulfonyl
Vi	vinyl

CHART 1. LIGAND AND CATALYST STRUCTURES USED IN TABLES

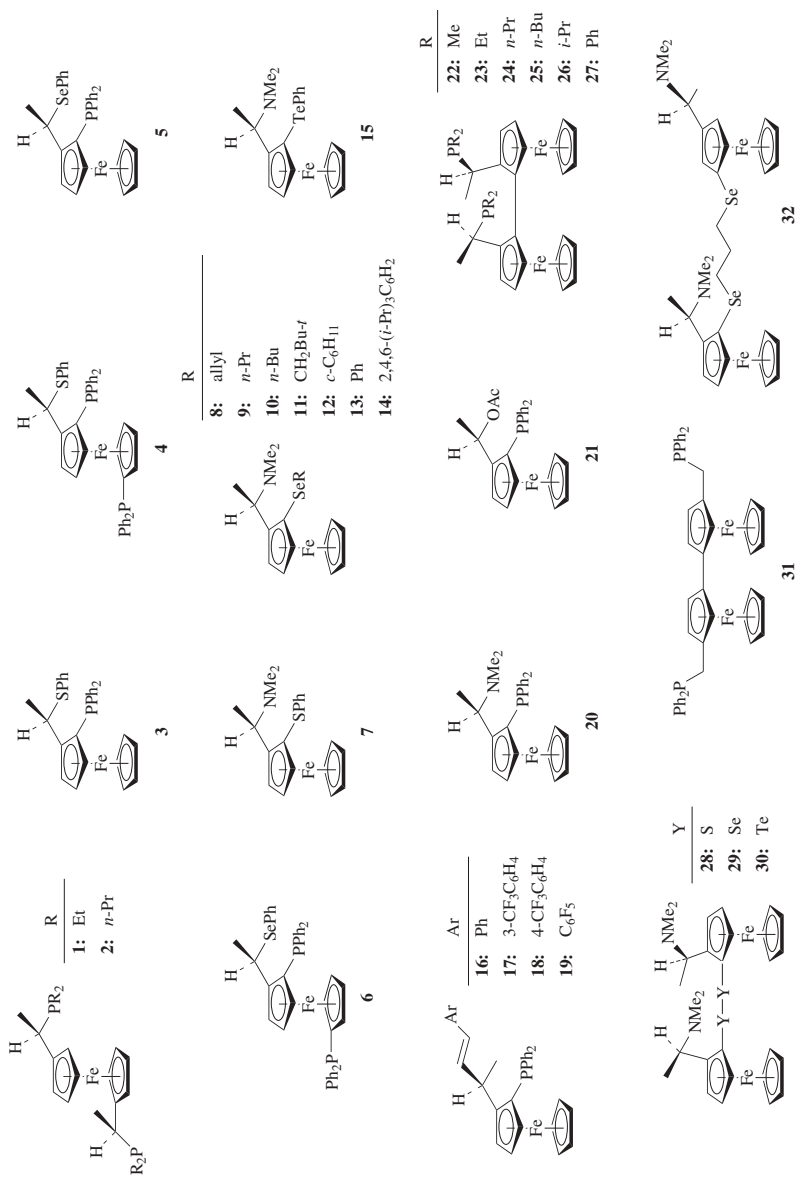
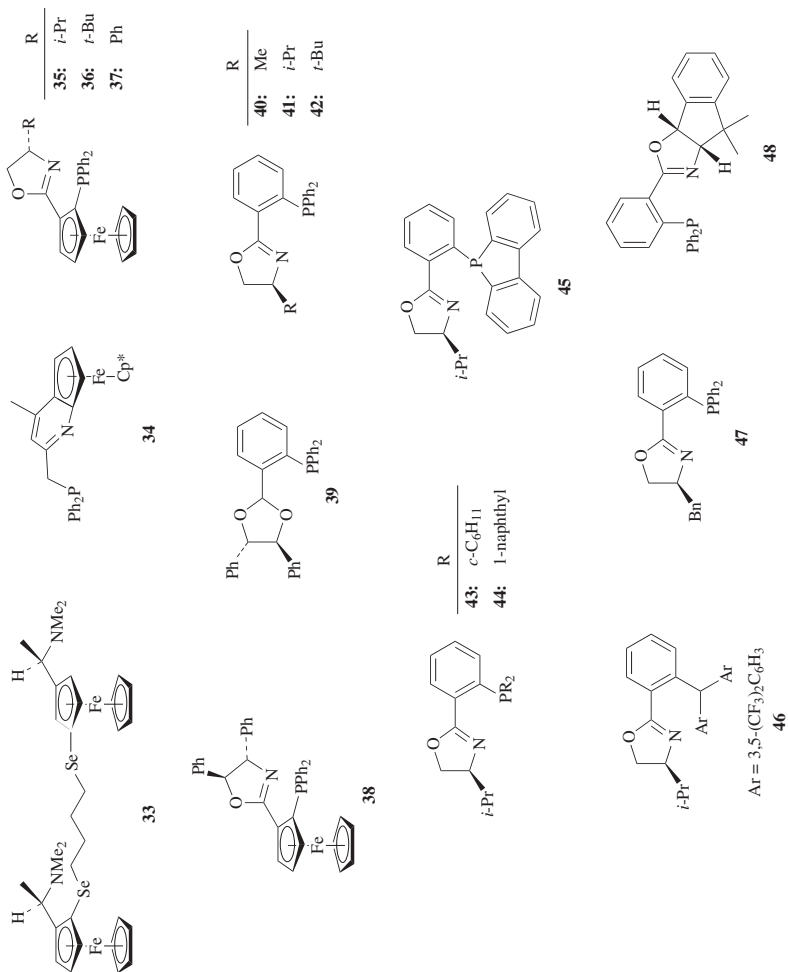


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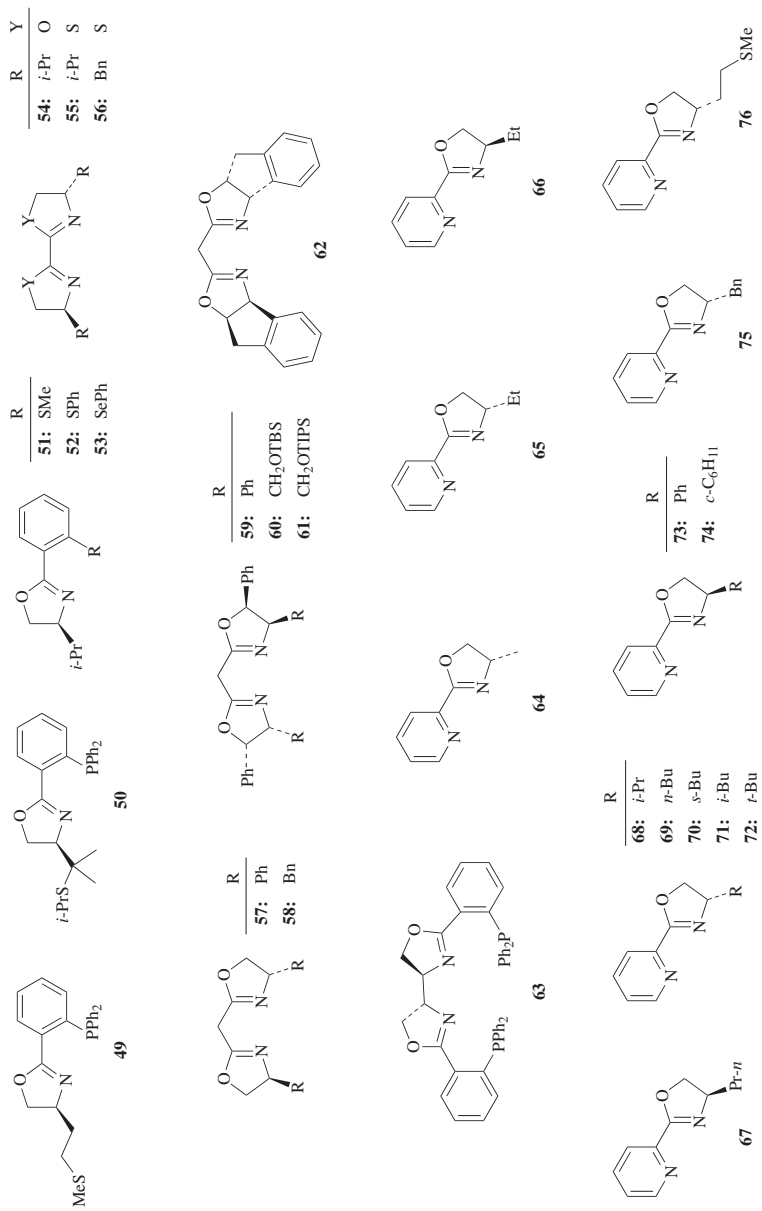
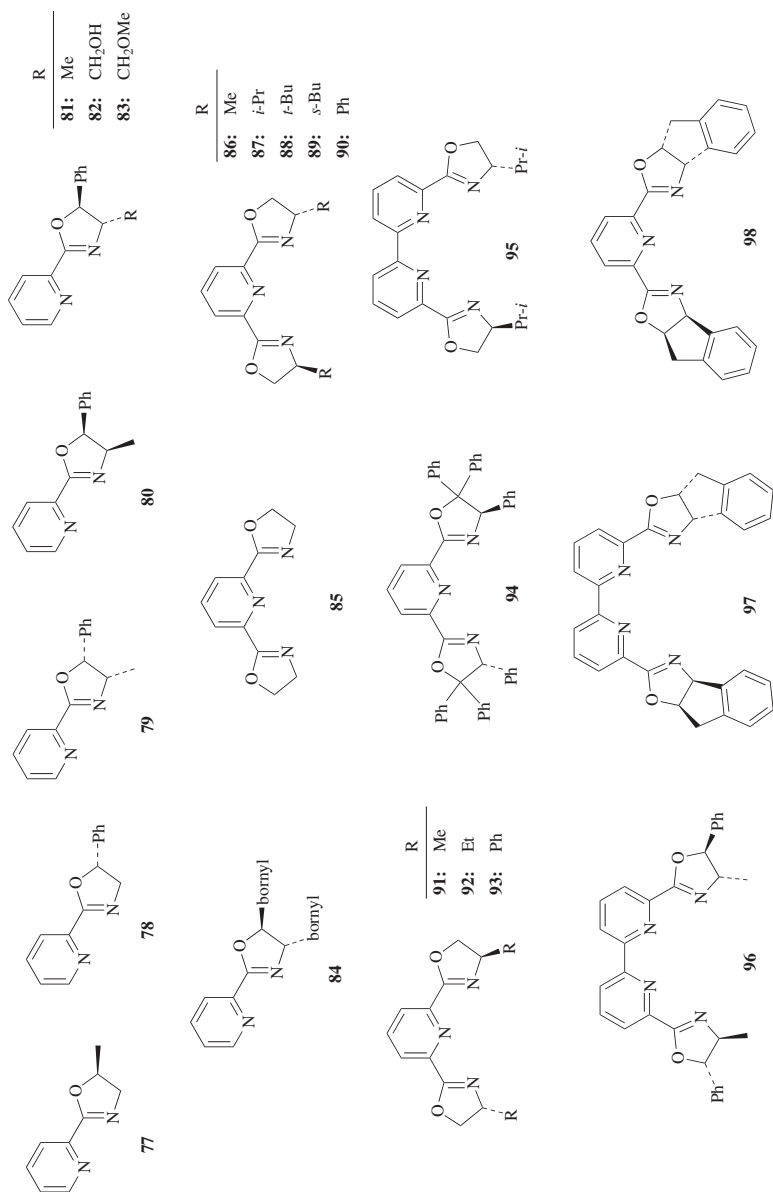


CHART 1. LIGAND AND CATALYST STRUCTURES USED IN TABLES (Continued)



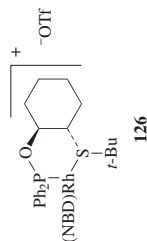
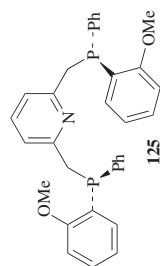
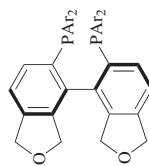
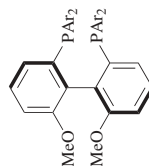
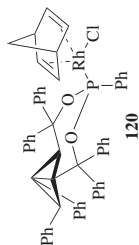
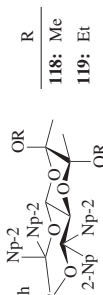
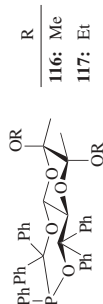
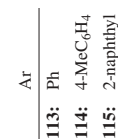
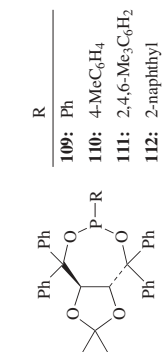
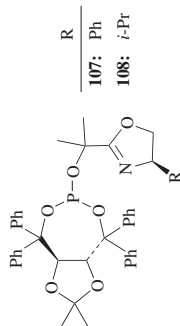
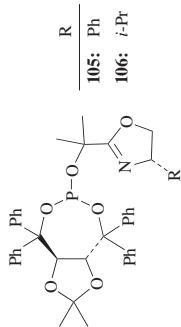
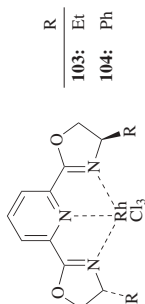
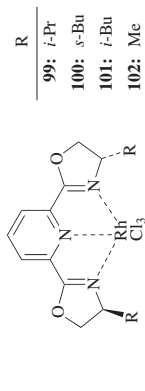
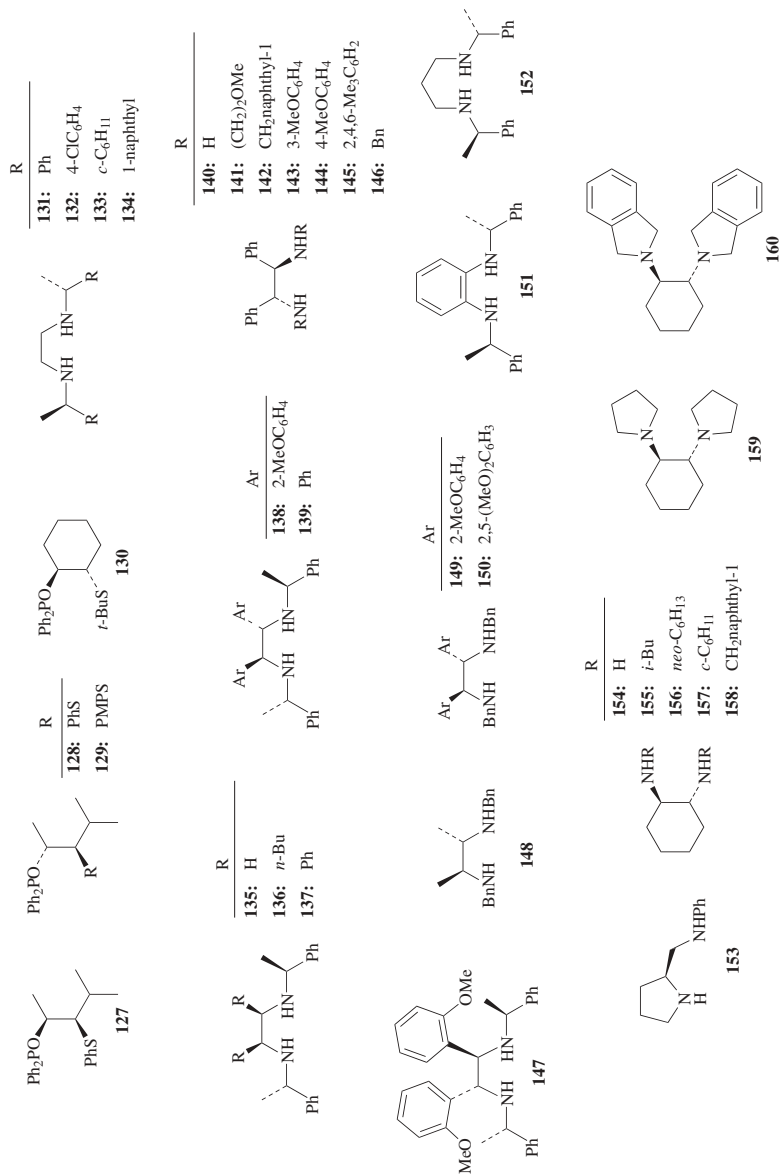


CHART 1. LIGAND AND CATALYST STRUCTURES USED IN TABLES (Continued)



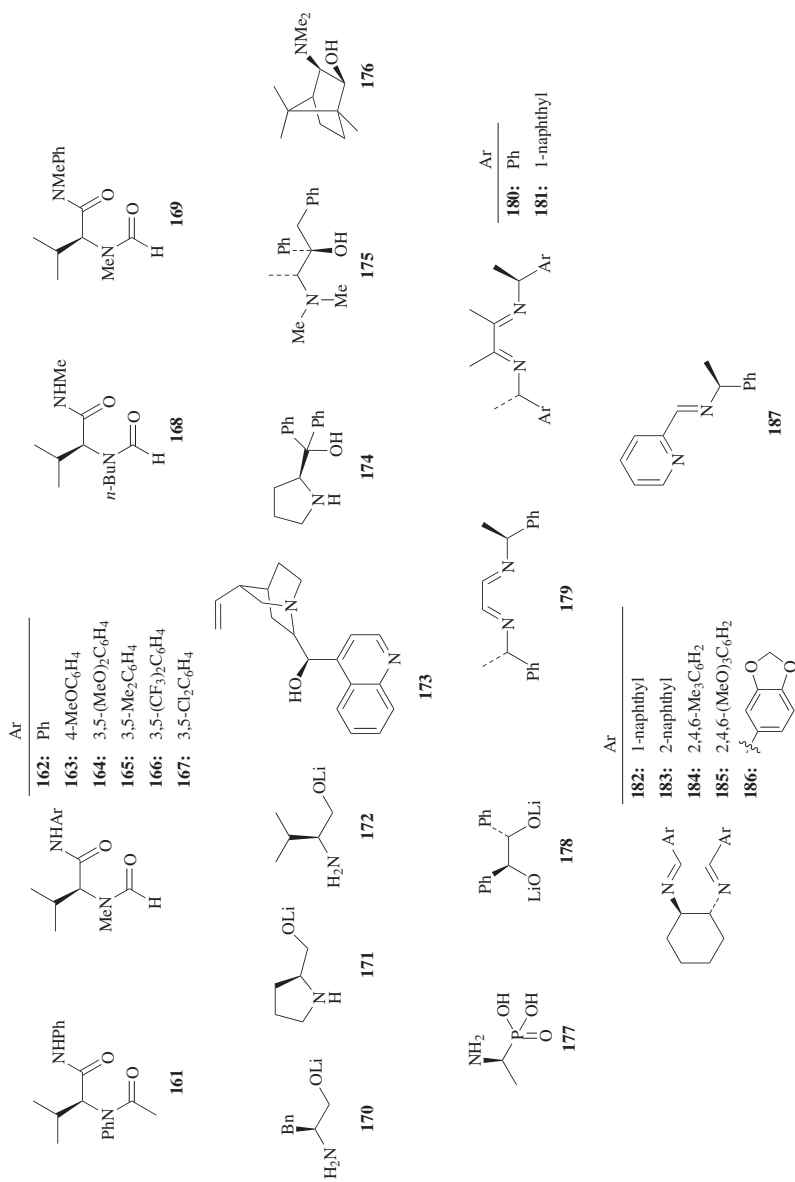
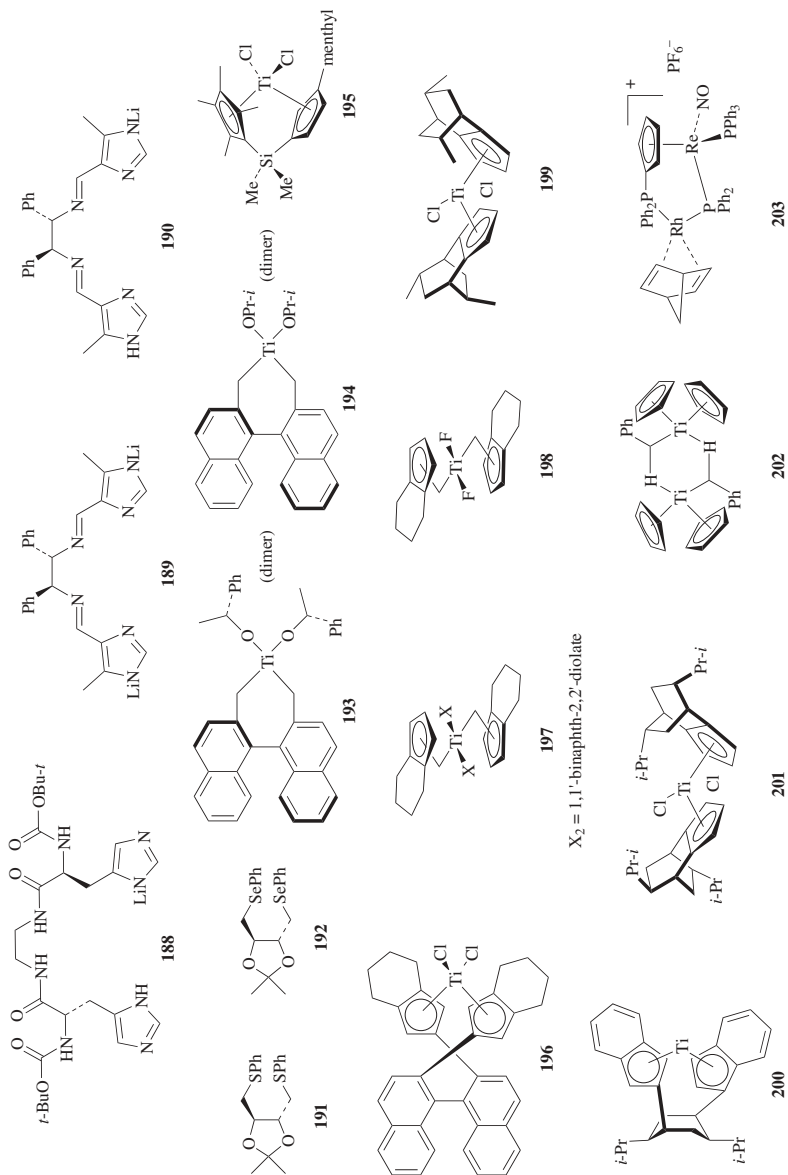
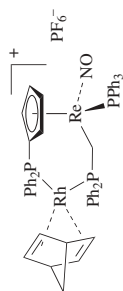
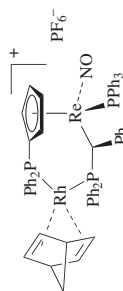


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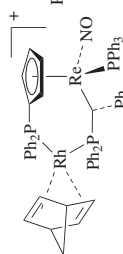




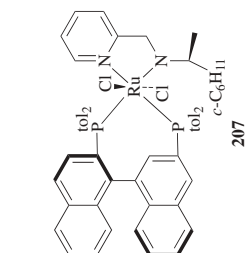
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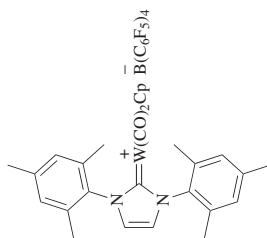
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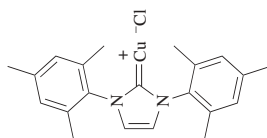
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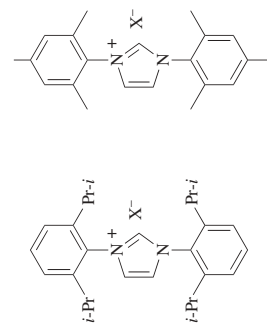
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208

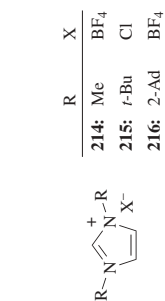


209



210: X = BF₄
211: X = Cl

212: X = BF₄
213: X = Cl



R

X

214: Me

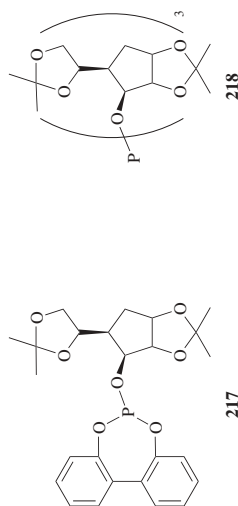
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216: 2-Ad

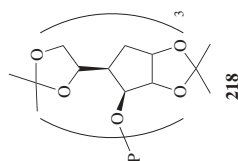
BF₄

Cl

BF₄



217



218

CHART 1. LIGAND AND CATALYST STRUCTURES USED IN TABLES (Continued)

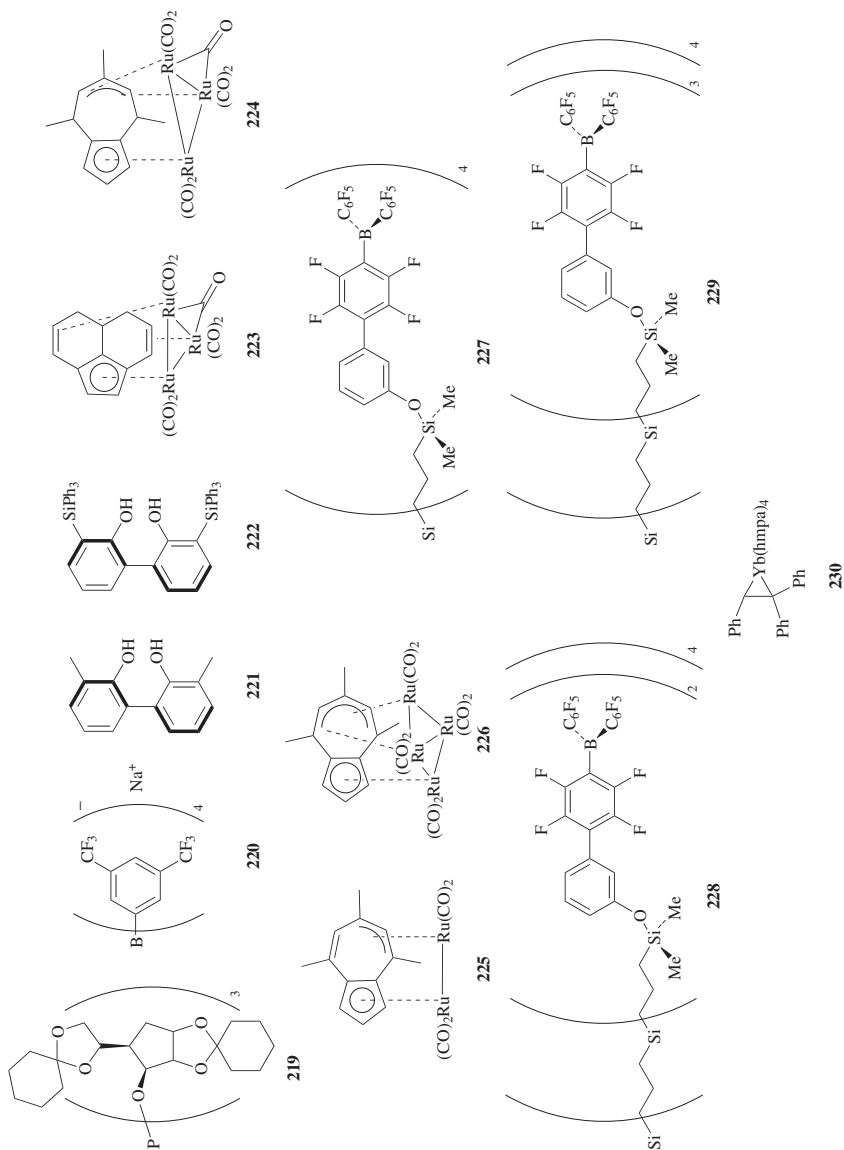


CHART 2. ORGANOSILANE COMPOUND DESIGNATIONS USED IN TABLES

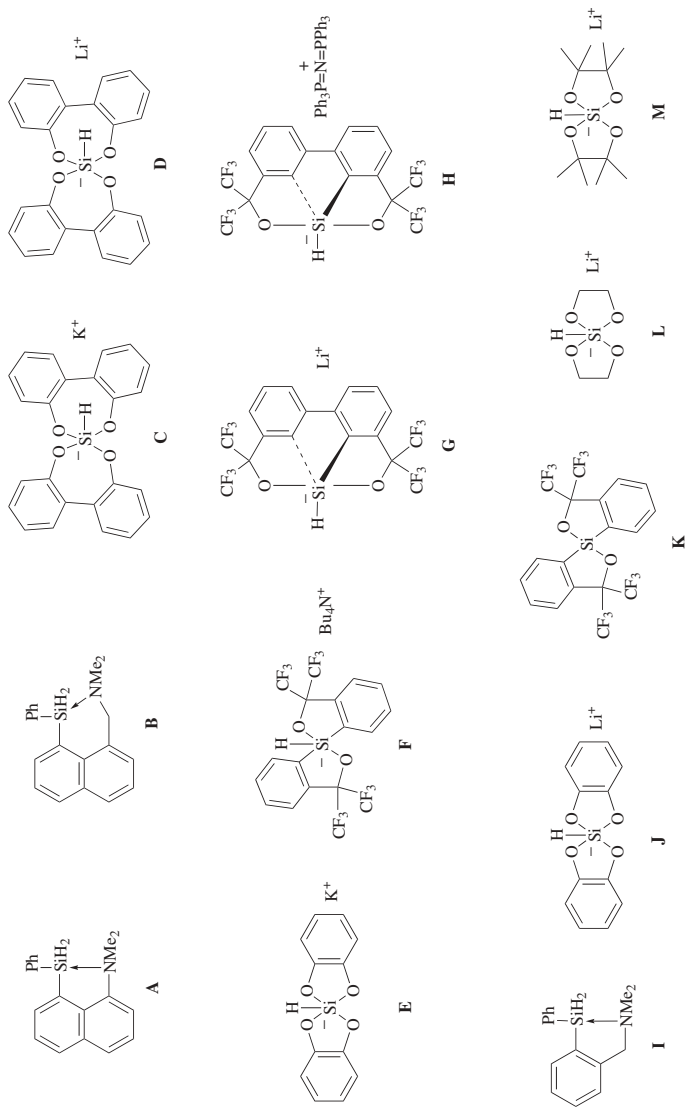




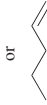




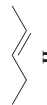
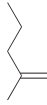
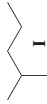







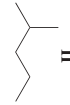
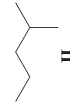



TABLE 1. ORGANOSILANE REDUCTION OF ALKENES

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.																																			
C ₄₋₆ 	Et ₃ SiH (x eq), TFA, 50°	R	234																																			
	x Time																																					
	1 10 h	(80)																																				
	2 75 h	(13)																																				
	2 75 h	(0)																																				
C ₅  SC ₄ H _{9-n}	2 20 h	(15)																																				
	PhSiH ₃ , 202		(—)	687																																		
 or 	Et ₃ SiH (1 eq), TFA (2 eq), 50°, 10 h		(—)	203																																		
	Et ₃ SiD (1 eq), TFA (2 eq), 50°, 24 h	D 	(90)	221																																		
	Et ₃ SiH (1 eq), TFA (2 eq), rt, 30 min		(—)	232																																		
	Et ₃ SiH, TFA (x eq)	 I +  II		233																																		
		<table><tr><th>x</th><th>Time</th><th>Temp</th></tr><tr><td>2.5</td><td>0.1 h</td><td>0°</td></tr><tr><td>4</td><td>0.5 h</td><td>20°</td></tr><tr><td>4</td><td>1 h</td><td>20°</td></tr><tr><td>2.5</td><td>1.5 h</td><td>20°</td></tr><tr><td>2.5</td><td>4 h</td><td>20°</td></tr><tr><td>2.5</td><td>15 h</td><td>20°</td></tr></table>	x	Time	Temp	2.5	0.1 h	0°	4	0.5 h	20°	4	1 h	20°	2.5	1.5 h	20°	2.5	4 h	20°	2.5	15 h	20°	<table><tr><th>I</th><th>II</th></tr><tr><td>(—)</td><td>(—)</td></tr><tr><td>(41)</td><td>(6.3)</td></tr><tr><td>(40)</td><td>(10.8)</td></tr><tr><td>(35)</td><td>(2.8)</td></tr><tr><td>(39)</td><td>(6)</td></tr><tr><td>(31)</td><td>(10)</td></tr></table>	I	II	(—)	(—)	(41)	(6.3)	(40)	(10.8)	(35)	(2.8)	(39)	(6)	(31)	(10)
x	Time	Temp																																				
2.5	0.1 h	0°																																				
4	0.5 h	20°																																				
4	1 h	20°																																				
2.5	1.5 h	20°																																				
2.5	4 h	20°																																				
2.5	15 h	20°																																				
I	II																																					
(—)	(—)																																					
(41)	(6.3)																																					
(40)	(10.8)																																					
(35)	(2.8)																																					
(39)	(6)																																					
(31)	(10)																																					

C ₅₋₁₆			Et ₃ SiH (2 eq), AlCl ₃ (1.0 eq), HCl, CH ₂ Cl ₂ , rt				136
			R ₃ SiH (1 eq), TFA, 50°, 20 h				688
C ₆			Et ₃ SiH (1.2 eq), 65% HClO ₄ , CH ₂ Cl ₂ , 20°, 30 min				214
			Et ₃ SiH (1.1-1.2 eq), HCO ₂ H, HOAc, KU-1, 55°, 5 h				208
			Et ₃ SiH (1.1-1.2 eq), HCO ₂ H, KU-1, 55°, 5 h				208
			Et ₃ SiH, TMSOTf, CD ₂ Cl ₂ , -75°, 5 min				216
			Et ₃ SiH (1 eq), TFA (2 eq), 50°, 10 h				203

TABLE I. ORGANOSILANE REDUCTION OF ALKENES (Continued)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₆	Et ₃ SiH (1 eq), TFA (2 eq)	 I	222
	Temp Time		
	20° 400 h	(75)	
	50° 3 h	(48)	
	50° 6 h	(67)	
	50° 24 h	(87)	
	80° 24 h	(80)	
	Et ₃ SiH, TMSOTf, CD ₂ Cl ₂ , -75°, 5 min	I (93) ^a	216
	Et ₃ SiD (1 eq), TFA (2 eq), 50°, 24 h	D  D	221
	Et ₃ SiH, TMSOTf, CD ₂ Cl ₂ , -75°, 5 min	(96) ^a	216
 	Et ₃ SiH (1 eq), TFA (2 eq), rt, 72 h	 I +  II +  I + II (80)	232
	Et ₃ SiH, TFA (x eq)	 I +  II +  I + II	233
	x Time Temp		
	2 0.5 h -10°	(78) (0)	
	3 0.5 h -10°	(59) (0.5)	
	2 3 h 20°	(52) (2)	
	2 50 h 20°	(40) (—)	
	Et ₃ SiD (1 eq), TFA (2 eq), -10°, 0.5 h	D  D (80)	221








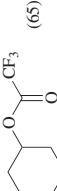
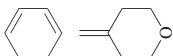




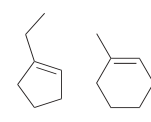
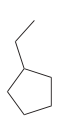
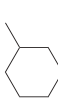

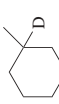





		Et_3SiH (2 eq), TFA (4 eq), 20°, 90 h	(65)	233								
		Et_3SiH (1 eq), TFA (2 eq), 50°, 10 h	(—)	203								
		Et_3SiD (1 eq), TFA (2 eq), 50°, 50 h	(60)	221								
		EtCl_2SiH (2 eq), AlBr_3 (1 eq), PTSA (1 eq), 40°, 2 h	(23)	192								
	I	EtCl_2SiH (2 eq), AlCl_3 (1 eq), PTSA (1 eq), 40°, 2 h	I (17)	192								
	I (100)	PMHS, Pd/C, EtOH, 80°	I (100)	316								
	I (—)	PhSiH_3 , 202		687								
		Et_3SiH (10.2 eq), TFA (13.2 eq), 20°, 24 h	(65)	230								
		Et_3SiH (x eq), AlCl_3 (3 eq), HCl , CH_2Cl_2 , rt	I	136								
	<table data-bbox="756 927 859 1039"><tr><th>x</th><th>Time</th></tr><tr><td>3</td><td>3.5 h</td></tr><tr><td>4</td><td>1 h</td></tr><tr><td>5</td><td>3 h</td></tr></table>	x	Time	3	3.5 h	4	1 h	5	3 h		(23)	
x	Time											
3	3.5 h											
4	1 h											
5	3 h											
			(40)									
			(41)									
	I (40)	Et_3SiH (3 eq), AlCl_3 (2 eq), HCl , 20°, 1 h	I (40)	146								
		Et_3SiH (5 eq), AlCl_3 (2.5 eq), HCl , CH_2Cl_2 , rt, 3 h	I (35)	136								

TABLE 1. ORGANOSILANE REDUCTION OF ALKENES (Continued)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et ₃ SiH (1.1-1.2 eq), HCO ₂ H, KU-1, 55°, 5 h	 (100)	208
	Et ₃ SiH (0.87 eq), TFA, rt, 120 h	 (78)	202
	Et ₃ SiH (1 eq), TFA (2 eq), 50°, 10 h	 I (—)	203
	Et ₃ SiD (1 eq), TFA (2 eq), 50°, 24 h	 (80)	221
	Et ₃ SiH (1 eq), TFA (x eq)	 I	203
	x Temp Time		
	1.5 50° 10 h	(40)	
	2 50° 10 h	(67)	
	2 20° 120 h	(73)	
	2.5 50° 10 h	(72)	
	10 20° 120 h	(78)	
	Et ₃ SiH (1 eq), TFA (8 eq), O ₂ NC ₆ H ₅ , 50°, 3 h	 I (92)	207
	Et ₃ SiO(EtHSiO) _n SiEt ₃ (0.1 eq), TFA (8 eq), O ₂ NC ₆ H ₅ , 50°, 3 h	 I (94)	207
	Et ₃ SiH (1.2 eq), 65% HClO ₄ , CH ₂ Cl ₂ , 20°, 30 min	 I (97)	214
	Et ₃ SiH (1.4 eq), HCl (xs), AlCl ₃ (0.2 eq), CH ₂ Cl ₂ , rt	 I (100)	213

Solvent	Time	Temp	96% H ₂ SO ₄	90% H ₂ SO ₄
EtOH	1.5 h	60°	(100)	(—)
<i>n</i> -BuOH	2 h	rt	(72)	(62)
<i>n</i> -C ₈ H ₁₇ OH	2 h	rt	(65)	(63)
<i>n</i> -C ₁₂ H ₂₅ OH	2 h	60°	(73)	(—)
<i>n</i> -C ₁₂ H ₂₅ OH	3.5 h	60°	(—)	(65)
(<i>n</i> -Bu) ₂ O	2.5 h	rt	(—)	(61)
(<i>n</i> -C ₈ H ₁₇) ₂ O	2.5 h	rt	(—)	(69)
(<i>n</i> -C ₈ H ₁₇) ₂ O	2 h	60°	(68)	(70)
<i>n</i> -C ₄ H ₉ OC ₁₂ H ₂₅ - <i>n</i>	2 h	60°	(93)	(89)












KU-1, 55°, 5 h

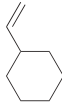
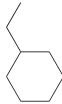

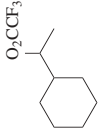

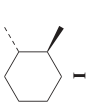



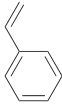
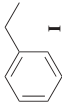
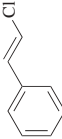
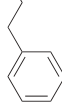
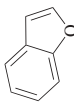
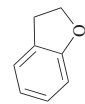

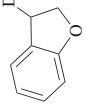

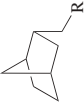
Solvent	
HCO ₂ H	(96)
HCO ₂ H, HOAc	(77)
HOAc	(37)
MeOH	(5)
CH ₂ Cl ₂	(0)

acid, 130°, 10 h

Acid	
CF ₃ CO ₂ H	(50)
ClF ₂ CCO ₂ H	(25)
Cl ₃ CCO ₂ H	(5)
Cl ₂ HCCO ₂ H	(0)
CH ₃ CO ₂ H	(0)
4-MeC ₆ H ₄ SO ₃ H	(35)





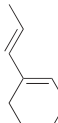
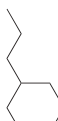
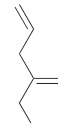
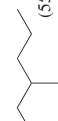
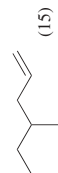
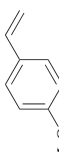
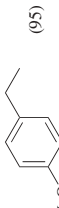


TABLE I. ORGANOSILANE REDUCTION OF ALKENES (Continued)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇ 	Ph ₂ SiH ₂ , O ₂ NC ₆ H ₅ , 130°	 (98)	193
	Et ₃ SiO(EtHSiO) ₆ SiEt ₃ (0.25 mol%), TFA, 50°, 20 h	I (100)	207
	Et ₃ SiO(EtHSiO) ₆ SiEt ₃ (0.1 mol%), TFA (x eq), solvent, 20°	I	207
	x Solvent Time 3 CHCl ₃ 5 h 5 4-O ₂ NC ₆ H ₅ 5 h	(52) (89)	
	EtCl ₂ SiH (2 eq), AlCl ₃ (1 eq), PTSA (1 eq), 40°, 2 h	I (65)	192
 or  or 	PhSiH ₃ , 202	I (—)	687
	Et ₃ SiH (5 eq), TFA (10 eq), 20°, 24 h	 (3.5) +  CF ₃ CO ₂ (—)	230
	Et ₃ SiH (5 eq), TFA (10 eq), BF ₃ •OEt ₂ (0.4 eq), 20°, 24 h	I (22)	230
	PhSiH ₃ , 202	I (—)	687
	Et ₃ SiH (10.2 eq), TFA (20.3 eq), 20°, 24 h	 O ₂ CCF ₃ +  O ₂ CCF ₃ + II + III + III = 62:20:17 (88)	230
C ₈ 	PMHS, Pd/C, EtOH, 80°		316

			(20) +		230
	Et ₃ SiH (5.1 eq), TFA (13.1 eq), 20°, 24 h				
			+		229
	Et ₃ SiH (1 eq), TFA (2 eq), 20°	I		II	
				Time	I + II
				2 h	(13) 1.5
				24 h	(58) 1.3
				144 h	(72) 1.5
				240 h	(74) 1.5
				(45)	230
	Et ₃ SiH (5.1 eq), TFA (13.1 eq), 20°, 24 h				
				(—)	203
	Et ₃ SiH (1 eq), TFA (2 eq), 50°, 10 h	I			
	PhSiH ₃ , 202	I (—)			687
	PMHS-Pd nanocomposite, C ₆ H ₆ , rt, 4 h	I (95)			219
				(85)	219
	PMHS-Pd nanocomposite, C ₆ H ₆ , rt, 6 h				
					251
	Et ₃ SiH (1.5 eq), TFA (x eq), 3 h			x	Temp
				2.5	70° (54)
				3.5	60° (48)
				5	60° (66)
				(47)	251
	Et ₃ SiH (1.5 eq), CF ₃ CO ₂ D (2.5 eq), 60°, 7 h				
				R	(85)
	Et ₃ SiH (6.5 eq), TFA (12.1 eq), BF ₃ ·OEt ₂ (1 eq), 20°, 24 h			H	(80)
				Me	230

C_{8,9}

TABLE I. ORGANOSILANE REDUCTION OF ALKENES (Continued)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-18} 	Et_3SiH (2 eq), $PdCl_2$ (10 mol%), EtOH		220
R	Time		
$n-C_6H_{13}$	1 d	(100)	
$n-C_8H_{17}$	1 d	(90)	
$n-C_{10}H_{21}$	1.5 d	(97)	
$n-C_{12}H_{25}$	1 d	(73)	
$n-C_{14}H_{29}$	1.5 d	(97)	
$n-C_{16}H_{33}$	1 d	(96)	
C_9 	PMHS, Pd/C , EtOH, 80°	 (25)	316
	Et_3SiH , TFA	 I (—)	233
	Et_3SiH (2 eq), TFA (3 eq)	I (70)	231
	Et_3SiH (6.5 eq), TFA (12.1 eq), $BF_3 \cdot OEt_2$ (1 eq), 20° , 24 h	I (75)	230
	Et_3SiH (2 eq), TFA (3 eq)	 I (55) +  II (15)	231
	Et_3SiH (6.5 eq), TFA (12.1 eq), $BF_3 \cdot OEt_2$ (1 eq), 20° , 24 h	I (25) + II (—)	230
	PMHS-Pd nanocomposite, C_6H_6 , rt, 3 h	 (95)	219
	Et_3SiH (1 eq), TFA (8 eq), 60° , 10 h	 (73)	689

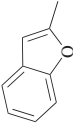
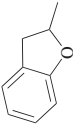
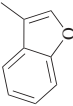
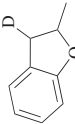
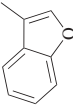
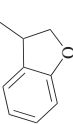
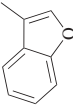
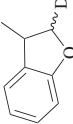
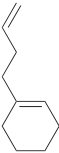
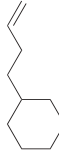
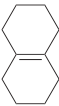
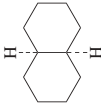
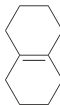
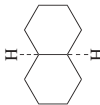
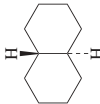
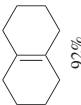
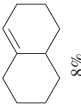


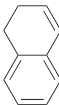
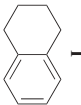
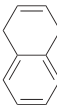

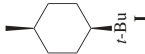
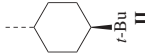
	Et_3SiH (1.5 eq), TFA (2.5 eq), 60°		Time 0.5 h (84) 2 h (91)	251
	Et_3SiH (1.5 eq), $\text{CF}_3\text{CO}_2\text{D}$ (2.5 eq), 60°, 2 h		(86)	251
	Et_3SiH (1.5 eq), TFA (2.5 eq), 60°		Time 0.2 h (84) 7 h (91)	251
	Et_3SiH (1.5 eq), $\text{CF}_3\text{CO}_2\text{D}$ (2.5 eq), 60°, 7 h		(60)	251
	Et_3SiH (2 eq), TFA (3 eq)		(65)	231
	R_3SiH (x eq), TFA (5 eq), rt, <5 d	 I + II	rel % I 37 40 42 35 54 58 72 77 83 93	204
	R_3Si x		I:II 0.59 0.67 0.72 0.54 1.17 1.38 2.57 3.35 4.88 13.3	
	$n\text{-BuH}_2\text{Si}$ 0.36			
	Et_2HSi 0.60			
	Et_3Si 1.1			
	(<i>i</i> -C ₅ H ₁₁) ₃ Si 1.1			
	(<i>n</i> -C ₅ H ₉) ₃ Si 1.1			
	Ph ₃ Si 1.1			
	(<i>n</i> -Bu) ₃ Si 1.1			
	(<i>i</i> -Bu) ₂ HSi 0.55			
	(<i>i</i> -Bu) ₂ MeSi 1.1			
	(<i>i</i> -Bu) ₃ Si 1.1			

TABLE 1. ORGANOSILANE REDUCTION OF ALKENES (Continued)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.																					
	R_3SiH (1.5 eq), acid	 + 	212																					
	<table><tr><th>R_3Si</th><th>Acid</th></tr><tr><td>Et_3Si</td><td>TFA</td></tr><tr><td>Et_3Si</td><td>$n\text{-C}_3\text{F}_7\text{CO}_2\text{H}$</td></tr><tr><td>$\text{Ph}_2\text{HSi}$</td><td>TFA</td></tr><tr><td>Ph_2MeSi</td><td>TFA</td></tr><tr><td>Ph_3Si</td><td>TFA</td></tr><tr><td>$(t\text{-Bu})_3\text{Si}$</td><td>TFA</td></tr></table>	R_3Si	Acid	Et_3Si	TFA	Et_3Si	$n\text{-C}_3\text{F}_7\text{CO}_2\text{H}$	Ph_2HSi	TFA	Ph_2MeSi	TFA	Ph_3Si	TFA	$(t\text{-Bu})_3\text{Si}$	TFA	<table><tr><th>I:II</th></tr><tr><td>1:2.9</td></tr><tr><td>1:4</td></tr><tr><td>1:1.5</td></tr><tr><td>1:1.3</td></tr><tr><td>1.8:1</td></tr><tr><td>13.3:1</td></tr></table>	I:II	1:2.9	1:4	1:1.5	1:1.3	1.8:1	13.3:1	
	R_3Si	Acid																						
	Et_3Si	TFA																						
	Et_3Si	$n\text{-C}_3\text{F}_7\text{CO}_2\text{H}$																						
Ph_2HSi	TFA																							
Ph_2MeSi	TFA																							
Ph_3Si	TFA																							
$(t\text{-Bu})_3\text{Si}$	TFA																							
I:II																								
1:2.9																								
1:4																								
1:1.5																								
1:1.3																								
1.8:1																								
13.3:1																								
 92% +  8%	Ph_3SiH (1.2 eq), TFA (6 eq), CH_2Cl_2 , rt, 24 h	I (57) + II (32)	127																					
	$(R)\text{-1-NpPhMeSiH}$, (96.2% opt. purity, 1 eq), TFA, CH_2Cl_2 , rt, 20 min	 (19) 2.05% ee	142																					
	Et_3SiH (1.6 eq) TFA, 50-60°, 1 h	 I (90)	224																					
	Et_3SiH (1.6 eq) TFA, 50-60°, 70 h	I (5)	224																					
	R_3SiH (x eq), TFA (5 eq), rt, <5 d	 I +  II	204																					



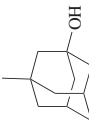

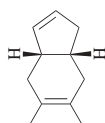
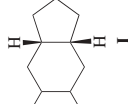
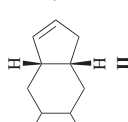


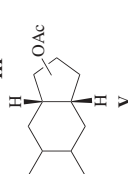

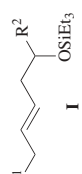
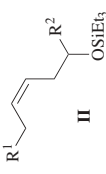
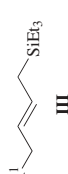
R_3Si	x	I	I:II		
<i>n</i> -BuH ₂ Si	1.1	(4)	0.04		
Et ₂ HSi	0.60	(8)	0.09		
Et ₃ Si	1.1	(10)	0.11		
(<i>i</i> -C ₃ H ₁₁) ₃ Si	1.1	(9)	0.10		
(<i>s</i> -Bu) ₃ Si	1.1	(16)	0.19		
(<i>i</i> -Bu) ₂ HSi	0.55	(16)	0.19		
Et ₃ SiH (1.5 eq), H ₂ SO ₄ (1.25 eq), CH ₂ Cl ₂ , rt, 6 h			+		II (14)
		I + II (76), I:II = 81:19			
Et ₃ SiH (1.5 eq), TFA (1.25 eq), CH ₂ Cl ₂ , rt, 6 h		I (29) +		III (45)	
Et ₃ SiH (1.5 eq), H ₂ SO ₄ /carbon, <i>n</i> -C ₈ H ₁₄ , rt, 6 h		I (25) + III (56)			
Et ₃ SiH (1.5 eq), H ₂ SO ₄ (1.25 eq), CH ₂ Cl ₂ , rt, 6 h		I (65) + III (15)			
Et ₃ SiH (1.5 eq), H ₂ SO ₄ /carbon, <i>n</i> -C ₈ H ₁₄ , rt, 6 h		I (11) + III (47)			
Et ₃ SiH (1.5 eq), H ₂ SO ₄ (1.25 eq), CH ₂ Cl ₂ , rt, 6 h		I + II + III (21), I:II:III = 29:66:5			
Et ₃ SiH (1.5 eq), H ₂ SO ₄ /carbon, <i>n</i> -C ₈ H ₁₄ , rt, 6 h		I (9) +		(12)	



TABLE I. ORGANOSILANE REDUCTION OF ALKENES (Continued)

Alkene	Conditions	Product(s) and Yield(s) (%)				Refs.			
<div>C₁₁</div> <div></div>	Et ₃ SiH (x eq), TFA (y eq)	<div></div> <div>I</div>	<div></div> <div>II</div>	<div></div> <div>III</div>	690				
		<div></div> <div>IV</div>	<div></div> <div>V</div>						
	x	y	Temp	Time	I	II	III	IV	
	5.5	1.3	rt	0.5 h	(2)	(18)	(5)	(65)	
	5.5	1.3	rt	6 h	(4)	(14)	(9)	(68)	
	5.5	1.3	rt	64 h	(15)	(1)	(6)	(67)	
	5.5	1.3	80°	1 h	(3)	(1)	(1)	(81)	
	5.5	1.3	80°	2 h	(12)	(—)	(2)	(69)	
	5.5	1.3	80°	9 h	(17)	(—)	(3)	(60)	
	13	5	80°	0.5 h	(2)	(5)	(3)	(76)	
	13	5	80°	17 h	(22)	(—)	(3)	(22)	
	13	5	80°	34 h	(41)	(—)	(7)	(17)	
<div>C₁₂₋₁₄</div> <div></div>	Et ₃ SiH (5 eq), Ni(cod) ₂ (20 mol%), PPh ₃ (40 mol%), MeC ₆ H ₅ , R ² CHO (1 eq), 50°	<div></div> <div>I</div>	<div></div> <div>II</div>	<div></div> <div>III</div>	691				




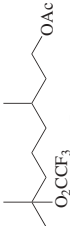
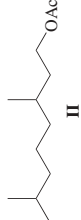
R ¹	R ²	Time	I:II	I + II	III																					
BnCH ₂	4-MeOC ₆ H ₄	20 h	100:0	(72)	(0)																					
BnCH ₂	4-MeO ₂ CC ₆ H ₄	19 h	100:0	(66)	(0)																					
MOMOCH ₂ C ₆ H ₄	4-MeOC ₆ H ₄	18 h	100:0	(76)	(0)																					
MOMOCH ₂ C ₆ H ₄	4-MeO ₂ CC ₆ H ₄	44 h	100:0	(59)	(0)																					
MOMOCH ₂ C ₆ H ₄	<i>n</i> -Pr	27 h	3:1	(71)	(0)																					
MOMOCH ₂ C ₆ H ₄	<i>i</i> -Pr	24 h	2:1	(81)	(0)																					
BnO(CH ₂) ₃	Ph	18 h	100:0	(63)	(7)																					
BnO(CH ₂) ₃	4-MeOC ₆ H ₄	19 h	100:0	(49)	(31)																					
BnO(CH ₂) ₃	4-MeO ₂ CC ₆ H ₄	44 h	100:0	(54)	(0)																					
BnO(CH ₂) ₃	<i>i</i> -Pr	18 h	100:0	(63)	(11)																					
 C ₁₂	Et ₃ SiH (1.3 eq), NH ₄ F (1.3 eq), TFA (5 eq), 0°, 0.5 h, rt, 3 h			(85)	135																					
	Et ₃ SiH (1.2 eq), 65% HClO ₄ , CH ₂ Cl ₂ , 20°, 30 min			(100)	214																					
	Et ₃ SiH (2 eq), TFA (2.5 eq), LiClO ₄ (x eq), <i>i</i> -PrNO ₂		 I +  II	<table><tr><th>I</th><th>II</th></tr><tr><td>(3)</td><td>(75)</td></tr><tr><td>(54)</td><td>(24)</td></tr><tr><td>(2)</td><td>(80)</td></tr><tr><td>(29)</td><td>(60)</td></tr><tr><td>(1)</td><td>(90)</td></tr><tr><td>(45)</td><td>(42)</td></tr></table>	I	II	(3)	(75)	(54)	(24)	(2)	(80)	(29)	(60)	(1)	(90)	(45)	(42)	205							
I	II																									
(3)	(75)																									
(54)	(24)																									
(2)	(80)																									
(29)	(60)																									
(1)	(90)																									
(45)	(42)																									
<table><tr><th>x</th><th>Temp</th><th>Time</th></tr><tr><td>0</td><td>80°</td><td>22 h</td></tr><tr><td>0</td><td>50°</td><td>22 h</td></tr><tr><td>0.1</td><td>50°</td><td>22 h</td></tr><tr><td>0.2</td><td>20°</td><td>22 h</td></tr><tr><td>1</td><td>20°</td><td>22 h</td></tr><tr><td>1</td><td>20°</td><td>3 h</td></tr></table>						x	Temp	Time	0	80°	22 h	0	50°	22 h	0.1	50°	22 h	0.2	20°	22 h	1	20°	22 h	1	20°	3 h
x	Temp	Time																								
0	80°	22 h																								
0	50°	22 h																								
0.1	50°	22 h																								
0.2	20°	22 h																								
1	20°	22 h																								
1	20°	3 h																								
Et ₃ SiH (2 eq), Cl ₂ CHCO ₂ H, LiClO ₄ (1 eq), <i>i</i> -PrNO ₂ , 20°, 48 h																										
I (20) + II (65)					205																					

TABLE 1. ORGANOSILANE REDUCTION OF ALKENES (Continued)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂ 	Et ₃ SiH (2 eq), TFA (2.5 eq), LiClO ₄ (1 eq), <i>i</i> -PrNO ₂ , 20°, 20 h	 (20)	205
	Et ₃ SiH, TFA	 (97)	223
	PMHS-Pd nanocomposite, C ₆ H ₆ , rt, 4 h	 (96)	219
	PMHS-Pd nanocomposite, C ₆ H ₆ , rt, 7 h	 (85)	219
C ₁₃ 	Et ₃ SiH (1.2 eq), TFA, CH ₂ Cl ₂ , rt, 30 min	 (—)	164
C ₁₄ 	Et ₃ SiH (1.3 eq), NH ₄ F (1.3 eq), TFA (5 eq), 0°, 0.5 h; rt, 3 h	 (93)	135
	Et ₃ SiH (1.25 eq), TFA (9 eq), CHCl ₃ , 0°, 1 h	 (62)	184
	PMHS-Pd nanocomposite, C ₆ H ₆ , rt, 4 h	 (94)	219

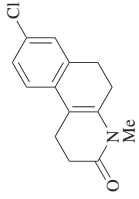
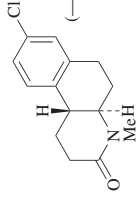
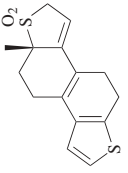
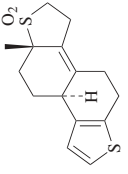
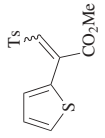
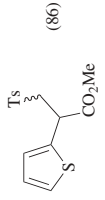


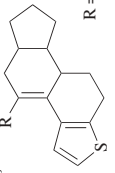
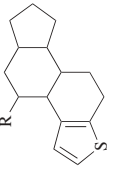
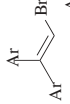
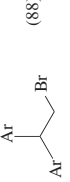
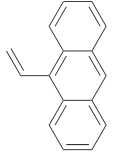
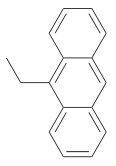
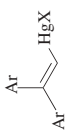
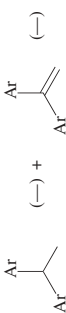

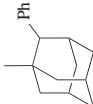
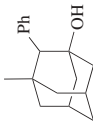
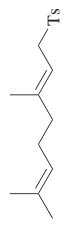
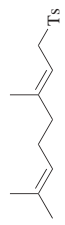
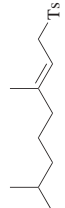


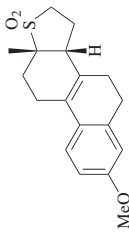
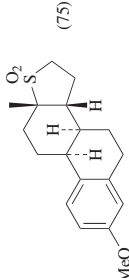
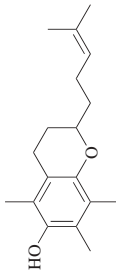
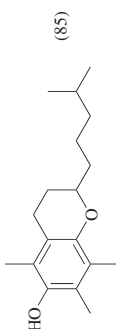
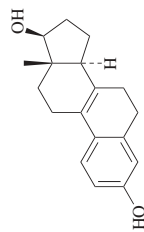
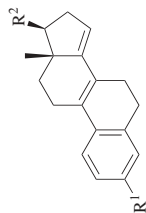
C ₁₄		Et ₃ SiH, TFA		(-) + (-)	692
C ₁₅		Et ₃ SiH, TFA, rt, 2 h		(68)	693
		Ph ₂ SiH ₂ (1.2 eq), AlCl ₃ (1 eq), CH ₂ Cl ₂ , 20°, 15 h		(86)	373
		Et ₃ SiH (1.2 eq), AlCl ₃ (1 eq), CH ₂ Cl ₂ , 20°, 15 h		I (86)	373
C ₁₅₋₁₆		Et ₃ SiH (1.1 eq), TFA (1.1 eq)		(-)	237
C ₁₆		Et ₃ SiH (1.5 eq), TFA (3 eq), CHCl ₃ , 0°, 1 h		(88)	184
		PMHS-Pd nanocomposite, C ₆ H ₆ , rt, 6 h		(92)	219

TABLE I. ORGANOSILANE REDUCTION OF ALKENES (Continued)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₆₋₁₈</p>  <p>Ar = 4-MeOC₆H₄; X = Cl, Br, CF₃CO₂</p>	Et ₃ SiH (1.5 eq), TFA (3 eq), CHCl ₃ , 0°, 1 h	 (-) + (-)	184
<p>C₁₇</p> 	Et ₃ SiH (1.5 eq), H ₂ SO ₄ (1.25 eq), CH ₂ Cl ₂ , rt, 6 h	 I  II (71) + (23)	243
	Et ₃ SiH (1.5 eq), H ₂ SO ₄ /carbon, <i>n</i> -C ₆ H ₁₄ , rt, 6 h	I (4) + II (47)	243
	Et ₃ SiH (2 eq), TFA (2.5 eq), LiClO ₄ (1 eq), <i>i</i> -PrNO ₂ , 20°, 20 h	 (7) +	(93) 205
	Et ₃ SiH (2 eq), TFA (2.5 eq), LiClO ₄ (1 eq), <i>i</i> -PrNO ₂ , 20°, 20 h	 (87)	205
<p>C₁₈</p> 	Et ₃ SiH, TFA, rt, 0°	 (75)	694
	Et ₃ SiH (2 eq), TFA (2.5 eq), LiClO ₄ (1 eq), <i>i</i> -PrNO ₂ , 20°, 20 h	 (85)	205

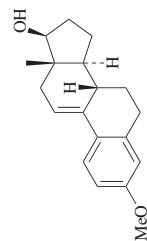
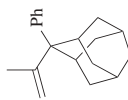


C₁₈₋₂₁



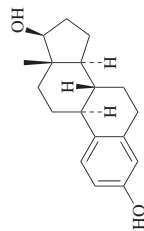
R ¹	R ²
OH	OH
OMe	OH
OMe	OH
OMe	OAc
OMe	OAc

C₁₉

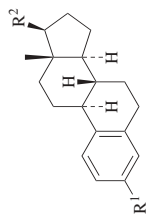


1. Et₃SiH, TFA

2. OH⁻, H₂O

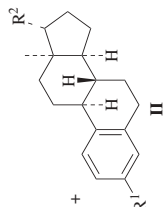


(96)

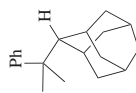


Solvent	I	II
C ₆ H ₆	(31)	(62)
C ₆ H ₆	(22)	(78)
CH ₂ Cl ₂	(34)	(66)
C ₆ H ₆	(20)	(40)
CH ₂ Cl ₂	(64)	(22)

Et₃SiH, TFA, solvent



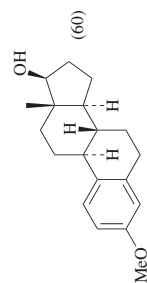
695



Et₃SiH (10 eq), MeSO₃H (1 eq),
CH₂Cl₂, -78°, 12 h; 0°, 10 h

(95)

140

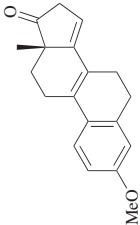
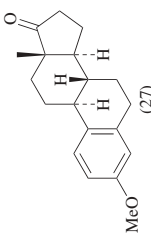
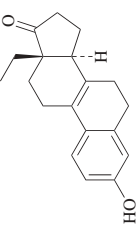
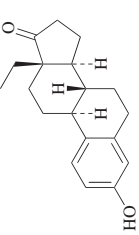
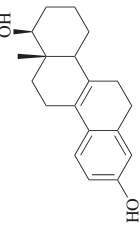
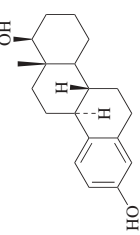
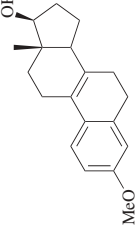
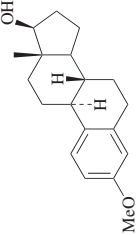
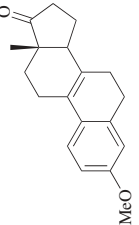
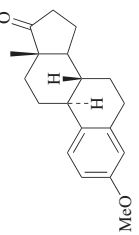


Et₃SiH, TFA

(60)

239

TABLE 1. ORGANOSILANE REDUCTION OF ALKENES (*Continued*)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₉	Et ₃ SiH, TFA	 (27)	241
	Et ₃ SiH, TFA	 (70)	226
	Et ₃ SiH, TFA	 (-)	240
	Et ₃ SiH, TFA	 (60)	226
	Et ₃ SiH, TFA	 (60)	226

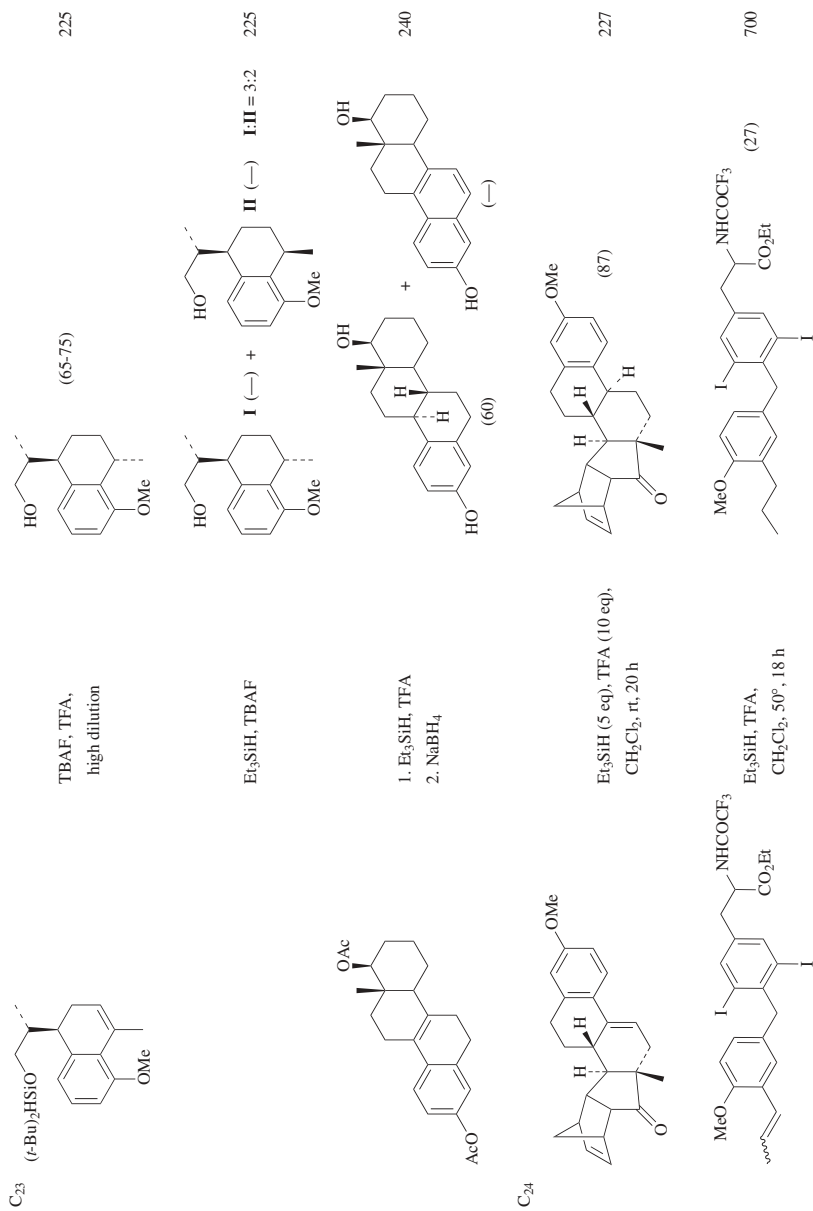
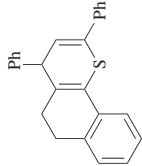
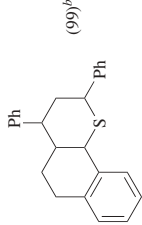
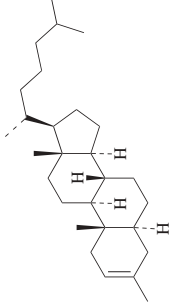
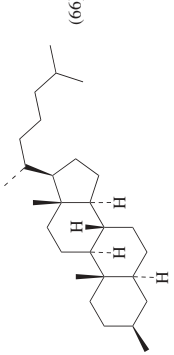
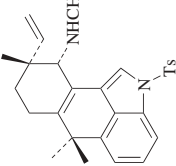
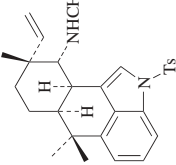
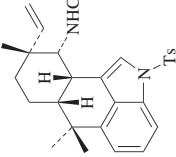

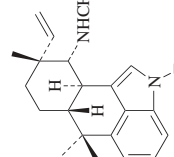


TABLE 1. ORGANOSILANE REDUCTION OF ALKENES (Continued)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₅	Et ₃ SiH (2 eq), TFA, rt, 7 min	 (99) ^b	228
 C ₂₈	Ph ₃ SiH (1.2 eq), TFA (6.5 eq), CH ₂ Cl ₂ , rt, 24 h	 (66)	127
 C ₂₈	Et ₃ SiH, TFA	 (2) +  (58)	701
 C ₂₈	Et ₃ SiH, TFA	 (19)	

^a The yield was determined by NMR spectroscopy.

^b The product was a single diastereomer of unknown stereochemistry.

TABLE 2. ORGANOSILANE REDUCTION OF ALKYNES






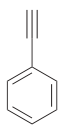
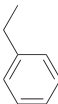
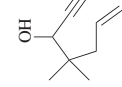
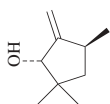
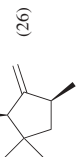
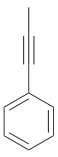
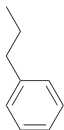
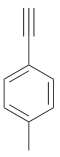
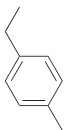
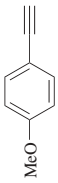
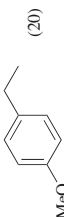
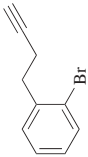
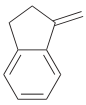
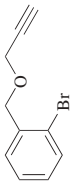
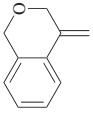
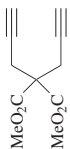
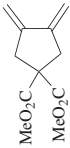
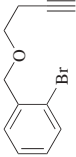
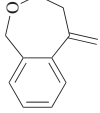
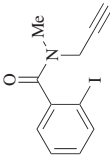
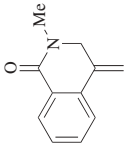
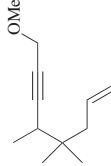
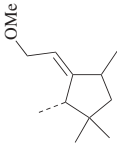
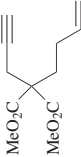
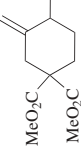
Alkyne	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (2 eq), TFA (3 eq), rt, 120 h	 (5)	244
	Et_3SiH (10 eq), AlCl_3 (0.5 eq), HCl , CH_2Cl_2 , 20°, 30 min	 (44) +  (7)	146
	Et_3SiH (5 eq), AlCl_3 (0.2 eq), HCl , CH_2Cl_2 , 20°, 90 min	 (40–50)	146
	Et_3SiH (5 eq), AlCl_3 (0.2 eq), HCl , CH_2Cl_2 , –40°, 300 min	I (55)	146
	Et_3SiH (2 eq), TFA (3 eq), rt, 120 h	I (30)	244
	Et_3SiH (1.2 eq), $\text{Pd}(\text{dppf})\text{Cl}_2$ (5 mol%), HCO_2H (1.2 eq), MeC_6H_5 , 70°, 2 h	 (52) +  (26)	246
	Et_3SiH (2 eq), TFA (3 eq), rt, 120 h	 (7)	244
	Et_3SiH (2 eq), TFA (3 eq), rt, 120 h	 (21)	244
	Et_3SiH (2 eq), TFA (3 eq), rt, 120 h	 (20)	244

TABLE 2. ORGANOSILANE REDUCTION OF ALKYNES (Continued)

Alkyne	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₀ 	Et ₃ SiH (2 eq), (Ph ₃ P) ₄ Pd (3 mol%), C ₅ H ₅ CO ₂ (2 eq), DMF, 60°, 20 h	 (62)	249
	Et ₃ SiH (2 eq), (Ph ₃ P) ₄ Pd (3 mol%), C ₅ H ₅ CO ₂ (2 eq), DMF, 80°, 4 h	 (54)	249
C₁₁ 	Et ₃ SiH (10 eq), Pd ₂ (dba) ₃ •CHCl ₃ (2.5 mol%), (<i>o</i> -tol) ₃ P (5 mol%), HOAc, rt, 25 min	 (34)	248
	Et ₃ SiH (2 eq), (Ph ₃ P) ₄ Pd (3 mol%), C ₅ H ₅ CO ₂ (2 eq), DMF, 80°, 3 h	 (48)	249
	Et ₃ SiH (2 eq), (Ph ₃ P) ₄ Pd (3 mol%), C ₅ H ₅ CO ₂ (2 eq), DMF, 100°, 12 h	 (82)	249
C₁₂ 	PMHS (10 eq), Pd ₂ (bpa) ₃ •CHCl ₃ (2.5 mol%), (<i>o</i> -tol) ₃ P (5 mol%), HOAc (1 eq), ClCH ₂ -CH ₂ Cl, rt	 (73)	245
	PMHS (10 eq), Pd ₂ (bpa) ₃ •CHCl ₃ (5 mol%), HOAc (1 eq), C ₆ H ₆ , rt	 (79)	245

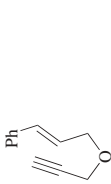
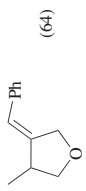
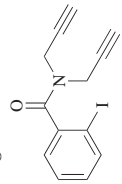
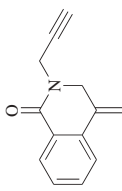

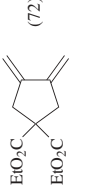
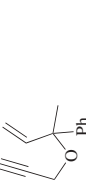
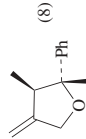






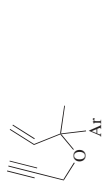
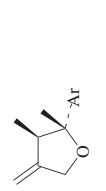


		Et_3SiH (1.2 eq), $\text{Pd}(\text{dppe})\text{Cl}_2$ (5 mol %), HCO_2H (1.2 eq), MeC_6H_5	246									
		Et_3SiH (2 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (3 mol %), Cs_2CO_3 (2 eq), DMF, 80° , 12 h	249									
		Et_3SiH (2 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (3 mol %), Cs_2CO_3 (2 eq), DMF, 80° , 4 h	249									
		Et_3SiH (1.2 eq), $\text{Pd}(\text{dppe})\text{Cl}_2$ (5 mol %), HCO_2H (1.2 eq), 1,4-dioxane, 70° , 10 h	246									
		Et_3SiH (2 eq), TFA (3 eq), rt, 120 h	244									
		Et_3SiH (12 eq), AlCl_3 (1.2 eq), HCl, CH_2Cl_2 , 20° , 195 min	146									
		Et_3SiH (97 eq), AlCl_3 (2.7 eq), HCl, CH_2Cl_2 , 20° , 170 min	146									
		Et_3SiH (1.2 eq), $\text{Pd}(\text{dppe})\text{Cl}_2$ (5 mol %), HCO_2H (1.2 eq), 1,4-dioxane, 70° , 10 h	246									
		<table><tr><th>Solvent</th><th>Temp</th><th>Time</th></tr><tr><td>1,4-dioxane</td><td>70°</td><td>10 h</td></tr><tr><td>MeC_6H_5</td><td>80°</td><td>3 h</td></tr></table>	Solvent	Temp	Time	1,4-dioxane	70°	10 h	MeC_6H_5	80°	3 h	246
Solvent	Temp	Time										
1,4-dioxane	70°	10 h										
MeC_6H_5	80°	3 h										

TABLE 2. ORGANOSILANE REDUCTION OF ALKYNES (Continued)

Alkyne	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₄</p> <p>Ar = 4-MeC₆H₄</p>	Et ₃ SiH (10 eq), Pd ₂ (dba) ₃ (10 mol%), PPh ₃ (10 mol%), HOAc (2 eq), MeC ₆ H ₅ , 50°, 2 h	<p>(70) +</p> <p>(8)</p>	247
<p>C₁₅</p>	Et ₃ SiH (1.2 eq), Pd(dppe)Cl ₂ (5 mol%), HCO ₂ H (1.2 eq), MeC ₆ H ₅ , 60°, 2 h	<p>(0)</p>	246
	Et ₃ SiH (1.2 eq), Pd(dppe)Cl ₂ (5 mol%), HCO ₂ H (1.2 eq), MeC ₆ H ₅ , 70°, 2 h	<p>(50) +</p> <p>(5)</p>	246
<p>Ar = 4-MeC₆H₄</p>	Et ₃ SiH (10 eq), Pd ₂ (dba) ₃ (10 mol%), PPh ₃ (10 mol%), HOAc (2 eq), MeC ₆ H ₅ , 50°, 2 h	<p>(5) +</p> <p>(47)</p>	247
<p>C₁₆₋₁₈</p>	Silane (10 eq), Pd ₂ (bpa) ₃ •CHCl ₃ (2.5 mol%), (o-tol) ₃ P (5 mol%), HOAc (1 eq), C ₆ H ₆ , rt	<p>(96)</p>	245
R ¹	Silane		
C ₆ H ₁₁	PMHS	(96)	
CH ₂ OTBS	PMHS	(88)	
CH ₂ OTBS	Et ₃ SiH	(59)	
CH(OAc) ₂	PMHS	(75)	
CH(OAc) ₂	Et ₃ SiH	(83)	


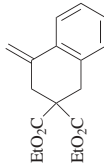
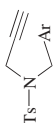
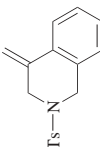
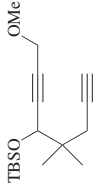
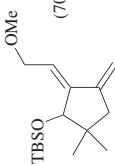
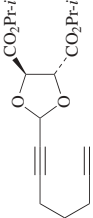
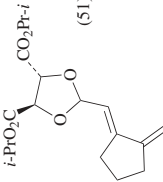
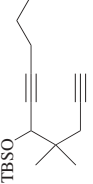
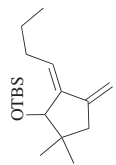

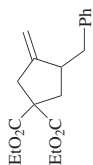
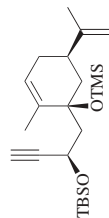
C ₁₇			Et ₃ SiH (2 eq), (Ph ₃ P) ₄ Pd (3 mol %), Cs ₂ CO ₃ (2 eq), DMF, 80°, 4 h	(85)	249
			Et ₃ SiH (2 eq), (Ph ₃ P) ₄ Pd (3 mol %), Cs ₂ CO ₃ (2 eq), DMF, 100°, 12 h	(65)	249
			Et ₃ SiH (10 eq), Pd ₂ (dba) ₃ •CHCl ₃ (2.5 mol %), (<i>o</i> -tol) ₃ P (5 mol %), HOAc, rt, 60 min	(70)	248
C ₁₈			Et ₃ SiH (10 eq), Pd ₂ (dba) ₃ •CHCl ₃ (2.5 mol %), (<i>o</i> -tol) ₃ P (5 mol %), HOAc, rt, 25 min	(51)	248
			Et ₃ SiH (10 eq), Pd ₂ (dba) ₃ •CHCl ₃ (2.5 mol %), (<i>o</i> -tol) ₃ P (5 mol %), HOAc, rt, 15 min	(60)	248
C ₁₉			Et ₃ SiH (1.2 eq), Pd(dppe)Cl ₂ (5 mol %), HCO ₂ H (1.2 eq), 1,4-dioxane, 60°, 2 h	(85)	246

TABLE 2. ORGANOSILANE REDUCTION OF ALKYNES (Continued)

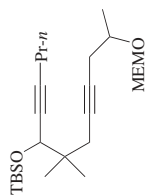
	Alkyne	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₉		Et ₃ SiH (10 eq), Pd ₂ (dba) ₃ •CHCl ₃ (2.5 mol%), (<i>o</i> -tol) ₃ P (5 mol%), HOAc, rt, 15 min		248
C ₂₀		(EtO) ₃ SiH, Cp*Ru(NCMe) ₃ PF ₆ , CH ₂ Cl ₂		477
C ₂₀		Et ₃ SiH (10 eq), Pd ₂ (dba) ₃ •CHCl ₃ (2.5 mol%), (<i>o</i> -tol) ₃ P (5 mol%), HOAc, rt, 20 min		248
C ₂₀		Et ₃ SiH (10 eq), Pd ₂ (dba) ₃ •CHCl ₃ (2.5 mol%), (<i>o</i> -tol) ₃ P (5 mol%), HOAc, rt, 3 min		248
C ₂₁		Et ₃ SiH (1.2 eq), Pd(dppe)Cl ₂ (5 mol%), HCO ₂ H (1.2 eq), MeC ₆ H ₅ , 60°, 2 h		246

C₂₃

241

(90)

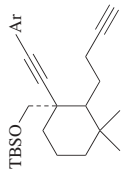
PMHS (10 eq), Pd₂(bpa)₃•CHCl₃ (2.5 mol %),
 (o-tol)₃P (5 mol %), HOAc (1 eq),
 ClCH₂CH₂Cl, rt

C₂₅

248

(83)

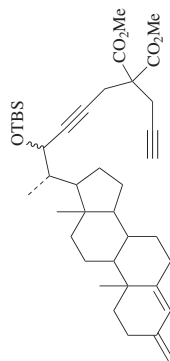
Et₃SiH (10 eq),
 Pd₂(dba)₃•CHCl₃ (2.5 mol %),
 (o-tol)₃P (5 mol %), HOAc, rt, 30 min

C₃₀

702

(79)

Et₃SiH (2 eq),
 (dba)₃PdCl₂•CHCl₃ (2.5 mol %),
 tri(2-furyl)phosphine (10 mol %),
 HCO₂H (2 eq), MeC₆H₅, 80°




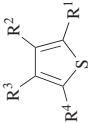
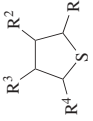
C₄₀

248



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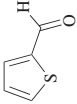

Et₃SiH (10 eq),
 Pd₂(dba)₃•CHCl₃ (2.5 mol %),
 (o-tol)₃P (5 mol %), HOAc, rt, 90 min

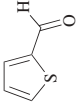

TABLE 3. ORGANOSILANE REDUCTION OF AROMATIC HYDROCARBONS

Aromatic Hydrocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₄	Et ₃ SiH (3 eq), AlCl ₃ (1.3 eq), CH ₂ Cl ₂ , 20°, 1.5 h	 I + II  (–) + (–)	259
	Et ₃ SiH (3 eq), TFA (30 eq), 20°, time	I + II	261
	36 min	I (10) II (17)	
	1026 min	(23) (42)	
	3993 min	(28) (48)	
	Et ₃ SiH (3 eq), TFA (30 eq), LiClO ₄ (1%), 20°, time	I + II	261
	Time	I II	
	11 min	(20) (31)	
	66 min	(30) (49)	
	232 min	(31) (53)	
 C ₄₊₂₈	Et ₃ SiH (3 eq), BF ₃ •OEt ₂ (0.057 mol%), 2 h	I (30) + II (50)	210
	R ₃ SiH (x eq), HCl (xs), AlCl ₃ (0.3 eq), CH ₂ Cl ₂ , rt	I	213
	R ₃ Si x Time		
	Et ₃ Si 5 15 h	(66)	
	Ph ₂ HSi 9.4 1 h	(39)	
	PhH ₂ Si 9.4 15 h	(43)	
	EtCl ₂ Si 1.7 15 h	(0)	
	Et ₃ SiH (x eq), TFA (y eq), 50°		257

R ¹	R ²	R ³	R ⁴	x	y	Time	
H	H	H	H	2	9	80 h	(60)
Cl	H	H	Cl	2	9	50 h	(—)
Me	H	H	H	2	7	20 h	(80)
Me	Me	Br	H	2	9	50 h	(—)
Et	H	H	Cl	3	8	100 h	(—)
CO ₂ H	H	H	Me	3	8	65 h	(—)
Me	Me	H	Me	2	7	20 h	(80)
(CH ₂) ₄ CO ₂ H	H	H	H	2	7	30 h	(65)
H	Ph	H	H	3	13	20 h	(70)
(CH ₂) ₅ CO ₂ Me	H	H	H	2	9	30 h	(65)
<i>t</i> -Bu	H	H	<i>t</i> -Bu	3	8	100 h	(15)
H	Ph	Ph	H	5	20	50 h	(70)
Ph	H	H	Ph	5	20	50 h	(—)
Ph	Ph	Ph	Ph	6	27	50 h	(—)

C ₅		Et ₃ SiH (x eq), TFA (y eq), BF ₃ •OEt ₂ (z eq), 20°, (addition of TFA/BF ₃ •OEt ₂ to mixture of the furan and Et ₃ SiH)		I	x	y	z	Time	I
					3	5	0	60 min	(4)
					4	8	0.2	4 min	(18)
					4	17	0.4	4 min	(31)

		Et ₃ SiH (x eq), TFA (y eq), BF ₃ •OEt ₂ (z eq), 20°, 4 min		I	x	y	z	Time	I
					4	17	0.4	(50)	
					10	50	0	(72)	
					10	50	0.4	(70)	

		Et ₃ SiH (4 eq), TFA (8 eq), 50°, 30 h		(65)					257
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







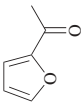

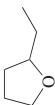
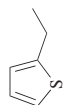
		Ph ₂ SiH ₃ (2 eq), Cp ₂ TiMe ₂ (10 mol%), 80°, 8 h		(94)					265
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TABLE 3. ORGANOSILANE REDUCTION OF AROMATIC HYDROCARBONS (Continued)

Aromatic Hydrocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₆	PhMeSiH ₂ (1.5 eq), Cp ₂ TiMe ₂ (10 mol%), 6 d	 I +  II +  III	264
	Temp	I II III	
	0°	(88) (0) (12)	
	24°	(85) (0) (15)	
	50°	(27) (17.2) (56)	
	60°	(19) (27) (49)	
	80°	(3) (57) (39)	
	PhMeSiH ₂ (1.5 eq), Cp ₂ TiMe ₂ (10 mol%), 80°, 6 d	III (30)	264
	PhMeSiH ₂ (2 eq), Cp ₂ TiMe ₂ (10 mol%), 80°, 8 h	II (51) + III (34)	265
	PhMeSiH ₂ (1.5 eq), Cp ₂ TiMe ₂ (10 mol%), 80°, 6 d	 I (53)	264
	Ph ₂ SiH ₂ (2 eq), Cp ₂ TiMe ₂ (10 mol%), 80°, 8 h	 I (83)	265
	Et ₃ SiH (10 eq), TFA (x eq), BF ₃ •OEt ₂ (y eq), 20°		211
	x y Time		
	30 0 20 h	(65)	
	50 0 2 h	(79)	
28 0.6 5 min	(80)		



Et₃SiH (3 eq), TFA (30 eq),
20°, 40 min



261

Et₃SiH (3 eq), TFA (10 eq),
p-TsOH (10 eq), 20°, 40 min

I (80)

261

Et₃SiH (3 eq), TFA (10 eq),
p-TsOLi (x eq),
LiClO₄ (y eq), 20°, 40 min

I (80)	x			y		
	1	0	(55)	1	0	(55)
	2	0	(60)	2	0	(60)
	3	0	(65)	3	0	(65)
	0	0.95	(78)	0	0.95	(78)
	0	1	(82)	0	1	(82)

261

Et₃SiH (1.1–1.2 eq),
HCO₂H, KU-1, 55°, 5 h
Et₃SiH (1.1–1.2 eq), HCO₂H,
HOAc, KU-1, 55°, 5 h

I (93)

208

Et₃SiH (3 eq), BF₃•OEt₂ (0.057 mol%),
50°, 4 h

I (80)

210

Et₃SiH (3 eq), AlCl₃ (0.3 eq),
CH₂Cl₂, 20°, 10 min

I (80)

259

Et₃SiH (3 eq), HCl (xs), AlCl₃ (0.3 eq),
CH₂Cl₂, rt, 10 min

I (80)

213

EtCl₂SiH (2 eq), AlBr₃ (3 eq),
PTSA (3 eq), 80°, 10 h

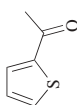
I (75)

192

Et₃SiH (5 eq), TFA (10 eq), 50°, 50 h

I (55)

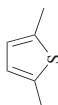
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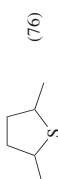
Et₃SiH (3 eq), AlCl₃ (1.3 eq),
CH₂Cl₂, 20°, 1.5 h

I (70)

259

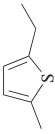
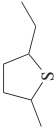
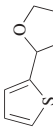
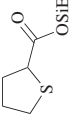
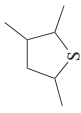
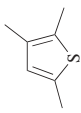

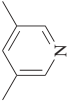
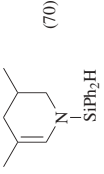
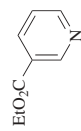
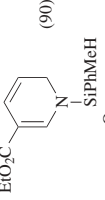
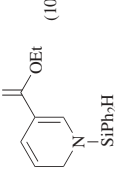


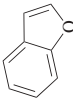

Et₃SiH (3 eq), HCl (xs),
AlCl₃ (0.3 eq), CH₂Cl₂, rt, 90 min



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TABLE 3. ORGANOSILANE REDUCTION OF AROMATIC HYDROCARBONS (Continued)

Aromatic Hydrocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇		 (75)	259
	Et ₃ SiH (3 eq), AlCl ₃ (0.3 eq), CH ₂ Cl ₂ , 20°, 1.5 h		
		 (45)	260
	Et ₃ SiH (2–5 eq), TFA (7–9 eq), 55°, 15 h		
	R ₃ SiH (x eq), HCl (xs), AlCl ₃ (0.3 eq), CH ₂ Cl ₂ , rt	 (61) (33) (0)	213
C ₈		 (60)	264
	PhMeSiH ₂ (1.5 eq), Cp ₂ TiMe ₂ (10 mol%), 80°, 8 d		
		 (70)	265
	Ph ₂ SiH ₂ (2 eq), Cp ₂ TiMe ₂ (10 mol%), 80°, 8 h		
		 (90)	264
C ₈	PhMeSiH ₂ (1.5 eq), Cp ₂ TiMe ₂ (10 mol%), 80°, 3 h	 (100)	265
	Ph ₂ SiH ₂ (2 eq), Cp ₂ TiMe ₂ (10 mol%), 80°, 8 h		

		251															
	<p>Et₃SiH (1.5 eq), TFA (x eq)</p> <table> <tr> <th>x</th><th>Temp</th><th>Time</th></tr> <tr> <td>2.5</td><td>70°</td><td>3 h</td></tr> <tr> <td>1.5</td><td>60°</td><td>3 h</td></tr> <tr> <td>3.5</td><td>60°</td><td>3 h</td></tr> <tr> <td>5</td><td>60°</td><td>3 h</td></tr> </table>	x	Temp	Time	2.5	70°	3 h	1.5	60°	3 h	3.5	60°	3 h	5	60°	3 h	<p>(54)</p> <p>(14)</p> <p>(48)</p> <p>(66)</p>
x	Temp	Time															
2.5	70°	3 h															
1.5	60°	3 h															
3.5	60°	3 h															
5	60°	3 h															
	Et ₃ SiH (1.5 eq), CF ₃ CO ₂ D (2.5 eq), 60°, 7 h	(47)															
	Et ₃ SiH (5 eq), TFA (15 eq), 20–50°, 1.5 h	(—)															
	Et ₃ SiH (3 eq), TFA (9 eq), 50°, 125 h	(55)															
	1. Et ₃ SiH (2.5 eq), TFA, 55°, 24 h 2. Et ₃ SiH (0.033 eq), 55°, 24 h	(30)															
	Et ₃ SiH (1–1.1 eq), TFA (7 eq), 50°, 20 h	(80)															
	Ph ₂ SiD ₂ (4 eq), TFA (11 eq), C ₆ H ₆ , 50°	(—)															
	Et ₃ SiH (1–1.1 eq), TFA (7 eq), 50°, 20 h	(90)															
	Ph ₂ SiD ₂ (4 eq), TFA (11 eq), C ₆ H ₆ , 50°	(—)															

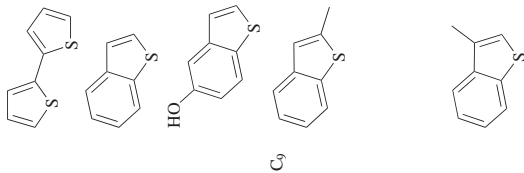
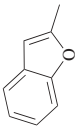
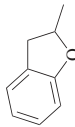
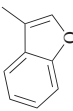
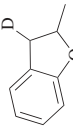
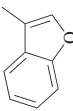
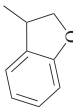
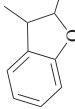
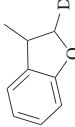
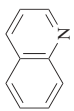
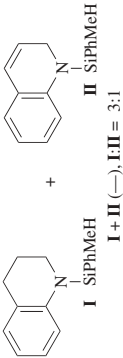
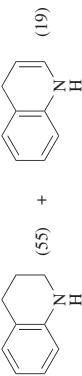



TABLE 3. ORGANOSILANE REDUCTION OF AROMATIC HYDROCARBONS (Continued)

Aromatic Hydrocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (1.5 eq), TFA (2.5 eq), 60°, 2 h	 (91)	251
	Et_3SiH (1.5 eq), $\text{CF}_3\text{CO}_2\text{D}$ (2.5 eq), 60°, 2 h	 (86)	251
	Et_3SiH (1.5 eq), TFA (2.5 eq), 60°, 2 h	 (62)	251
	Et_3SiH (1.5 eq), $\text{CF}_3\text{CO}_2\text{D}$ (2.5 eq), 60°, 7 h	 (60)	251
	PhMeSiH_2 (1.5 eq), Cp_2TiMe_2 (10 mol%), 80°, 36 h	 I + II (—), I:II = 3:1	264
	Ph_2SiH_2 (2 eq), Cp_2TiMe_2 (10 mol%), 80°, 8 h	 (55) + (19)	265
	PhMeSiH_2 (1.5 eq), Cp_2TiMe_2 (10 mol%), 200 psi H_2 , 80°, 48 h	 I (54)	264

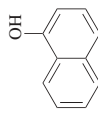
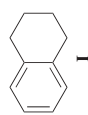
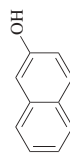
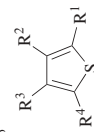
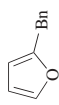
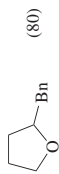
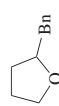
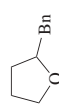
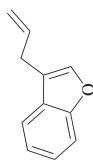
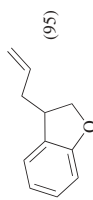
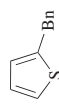
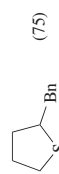
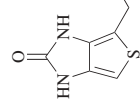
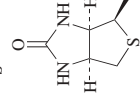

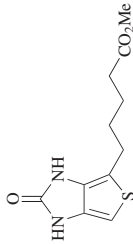
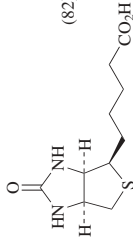
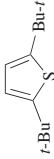
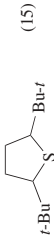
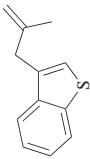
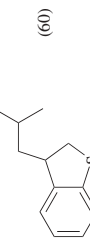
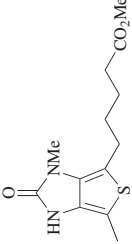
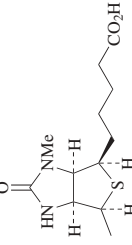
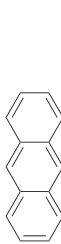
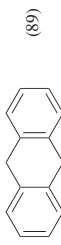
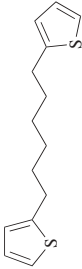
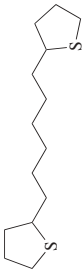
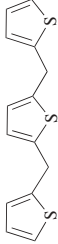
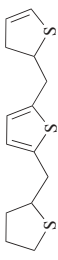
C ₁₀			Et ₃ SiH (1.3 eq), BF ₃ •OH ₂ (4-6 eq), CH ₂ Cl ₂ , rt, 4 h	(52)	217																								
C ₁₀₋₁₆		I (37)	Et ₃ SiH (1.3 eq), BF ₃ •OH ₂ (4-6 eq), CH ₂ Cl ₂ , rt, 10 h		217																								
		<table data-bbox="324 388 486 605"><thead><tr><th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th></tr></thead><tbody><tr><td>H</td><td>Ph</td><td>H</td><td>H</td></tr><tr><td>Ph</td><td>Ph</td><td>H</td><td>H</td></tr><tr><td>Ph</td><td>H</td><td>Ph</td><td>H</td></tr><tr><td>Ph</td><td>H</td><td>H</td><td>Ph</td></tr><tr><td>H</td><td>Ph</td><td>Ph</td><td>H</td></tr></tbody></table>	R ¹	R ²	R ³	R ⁴	H	Ph	H	H	Ph	Ph	H	H	Ph	H	Ph	H	Ph	H	H	Ph	H	Ph	Ph	H	Et ₃ SiH (3 eq), TFA, CHCl ₃ , 50°, 50 h		254
R ¹	R ²	R ³	R ⁴																										
H	Ph	H	H																										
Ph	Ph	H	H																										
Ph	H	Ph	H																										
Ph	H	H	Ph																										
H	Ph	Ph	H																										
C ₁₁			Et ₃ SiH (10 eq), TFA (50 eq)	(80)	211																								
			Et ₃ SiH (10 eq), TFA (28 eq), BF ₃ •OEt ₂ (0.6 eq), 20°, 5 min	(89)	211																								
			Et ₃ SiH, TFA, 20°, 1.5 h	(95)	252																								
			Et ₃ SiH (5 eq), TFA (9 eq), 50°, 30 h	(75)	257																								
			1. Et ₃ SiH, TFA, BF ₃ •OEt ₂ , Al ₂ O ₃ , 45-50°, 30 h 2. KOH, EtOH, 20°, 12 h	(80)	255																								
		I (5-8)	1. Et ₃ SiH, TFA, Al ₂ O ₃ , 45-50°, 30 h 2. KOH, EtOH, 20°, 12 h		255																								

TABLE 3. ORGANOSILANE REDUCTION OF AROMATIC HYDROCARBONS (Continued)

Aromatic Hydrocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₁	1. Et ₃ SiH, 50°, 30 h 2. KOH, EtOH, 20°, 12 h	 (82)	255, 256
 C ₁₂	Et ₃ SiH (3 eq), TFA, CHCl ₃ , 50°, 50 h	 (15)	254
 C ₁₃	Et ₃ SiH, TFA, 20°, 1.5 h	 (60)	252
 C ₁₄	1. Et ₃ SiH, 100°, 30 h 2. KOH, EtOH, 20°, 12 h	 (72)	255
 C ₁₅	Et ₃ SiH (1.3 eq), BF ₃ •OH ₂ (10 eq), CH ₂ Cl ₂ , rt, 1 h	 (89)	217
 C ₁₆	Et ₃ SiH (4 eq), TFA (8 eq), 50°, 30 h	 (70)	257
 C ₁₇	Et ₃ SiH (7 eq), TFA (13 eq), 50°, 50 h	 (60)	257

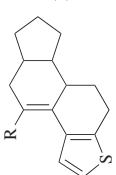
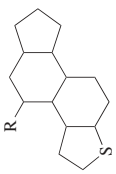
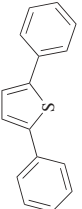
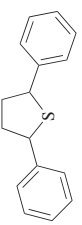
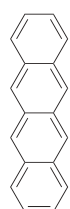
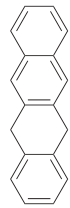
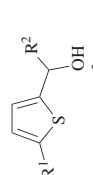
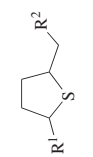
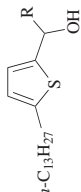
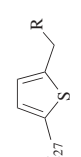
C ₁₅₋₁₆		Et ₃ SiH (xs), TFA (xs)		237
C ₁₆		Et ₃ SiH (3 eq), HCl (xs), AlCl ₃ (2 eq), CH ₂ Cl ₂ , rt		213
C ₁₈		Et ₃ SiH (1.3 eq), BF ₃ •OH ₂ (10 eq), CH ₂ Cl ₂ , rt, 4 h		217
C ₁₈₋₂₁		Et ₃ SiH, TFA, 50°, 48 h		258
C ₁₉₋₂₃		Et ₃ SiH, TFA, 50°, 48 h		258

TABLE 4. ORGANOSILANE REDUCTION OF HALOCARBONS

Halocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃ 	PMHS, (Ph ₃ P) ₄ Pd (5 mol%), MeCN, DMSO, Br ₂ N (1.4 eq), 110°, 3 h	 (35)	199
C ₄ 	Et ₃ SiH (1.4 eq), PdCl ₂ (5-10 mol%), rt, 1 h	 (81)	195
	Ph ₃ SiH, CH ₂ Cl ₂ , BF ₃ •OEt ₂ , rt	(—)	59
	Et ₃ SiH (1.4 eq), PdCl ₂ (5-10 mol%), rt, 1 h	 (>95)	195
C ₅ 	Et ₃ SiH (0.89 eq), AlCl ₃ , rt, 15 h	 (48.6)	185
	Et ₃ SiH (5 eq), AlCl ₃ (0.1 eq), HCl	 I (71)	146
	Et ₃ SiH (12 eq), AlCl ₃ (0.4 eq), C ₃ H ₁₂ , 40°, <1 h	I (71)	186
	Et ₃ SiH (1.4 eq), PdCl ₂ (5-10 mol%), rt, 10 min	 (>95)	195
	PhSiH ₃ (180 mol%), Mo(CO) ₆ (5 mol%), PPh ₃ (19 mol%), NaHCO ₃ (80 mol%), THF, 65°, 1.0 h	 I (>95)	197




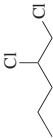

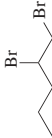
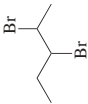


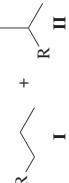







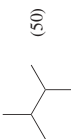






	<p>PhSiH₃ (160 mol%), Mo(CO)₆ (4 mol%), PPh₃ (16 mol%), NaHCO₃ (80 mol%), diglyme, 75°, 1.2 h</p>	I (100)	197
	<p>Et₃SiH (2.5 eq), AlCl₃ (0.25 eq), 20°, 30 min</p>	 I	189
	<p>Et₃SiH (2.5 eq), AlCl₃ (0.25 eq), 20°, 30 min</p>	I (70) +  (8)	189
	<p>Et₃SiH (2.5 eq), AlCl₃ (0.25 eq), 20°, 30 min</p>	I (72)	189
	<p>Et₃SiH (2.5 eq), AlCl₃ (0.25 eq), 20°, 30 min</p>	I (72)	189
	<p>Et₃SiH (2.5 eq), AlCl₃ (0.25 eq), 20°, 30 min</p>	I (85)	189
	<p>Et₃SiH (2.5 eq), AlCl₃ (0.25 eq), 20°, 30 min</p>	 I +  II	189
	<p>Et₃SiH (2.5 eq), AlCl₃ (0.25 eq), 20°, 30 min</p>	 I	189
	<p>Et₃SiH (0.89 eq), AlCl₃, rt, 15 h</p>	I (57)	185
	<p>Et₃SiH (5 eq), AlCl₃ (0.1 eq)</p>	I (~55%)	146

TABLE 4. ORGANOSILANE REDUCTION OF HALOCARBONS (Continued)

Halocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (5 eq), AlCl_3 (0.1 eq), HCl	I (64)	146
	Et_3SiH (0.89 eq), AlCl_3 , rt, 15 h	 (50)	185
	Et_3SiH (5 eq), AlCl_3 (0.1 eq)	 (~55%)	146
	Et_3SiH (5 eq), AlCl_3 (0.1 eq), HCl	 (71)	146
	Et_3SiH (5 eq), AlCl_3 (0.1 eq), HCl	I	146
	R_3SiH (1.3-1.5 eq), CH_2Cl_2 , AlCl_3 (25 mol%)	I (90)	188
	Et_3SiH (1.25 eq), AlCl_3 (0.25 eq), CH_2Cl_2 , 18-20°, 15 min	I (95)	187
	$\text{H}(\text{Ph}_2\text{Si})_4\text{H}$ (1.0 eq), AlCl_3 (1.0 eq), CH_2Cl_2 , 18-20°, 2 h	I (5)	187
	Et_3SiH (12 eq), AlCl_3 (0.4 eq), C_3H_{12} , 40°, <1 h	I (90)	186
	Et_3SiH (2.5 eq), AlCl_3 (0.25 eq), 20°, 30 min	I (67)	189
	Et_3SiH (2.5 eq), AlCl_3 (0.25 eq), 20°, 30 min	I (74)	189







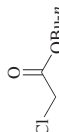

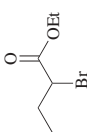
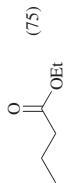





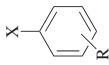





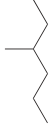
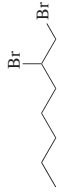
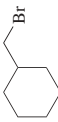

	I (74)	Et_3SiH (2.5 eq), AlCl_3 (0.25 eq), 20°, 30 min				189															
	I (88)	Et_3SiH (2.5 eq), AlCl_3 (0.25 eq), 20°, 30 min		<table><tr><th>x</th><th>y</th><th>Time</th></tr><tr><td>3</td><td>2</td><td>0.5 h (92)</td></tr><tr><td>2</td><td>2</td><td>0.5 h (75)</td></tr><tr><td>3</td><td>1.5</td><td>1.5 h (37)</td></tr><tr><td>3</td><td>0.75</td><td>20 h (0)</td></tr></table>	x	y	Time	3	2	0.5 h (92)	2	2	0.5 h (75)	3	1.5	1.5 h (37)	3	0.75	20 h (0)		189
x	y	Time																			
3	2	0.5 h (92)																			
2	2	0.5 h (75)																			
3	1.5	1.5 h (37)																			
3	0.75	20 h (0)																			
		Et_3SiH (x eq), AlCl_3 (y eq), HCl , CH_2Cl_2 , rt				136															
		Et_3SiH (1.4 eq), PdCl_2 (5-10 mol%), rt, 5 min			(>95)	195															
		PhSiH_3 (170 mol%), $\text{Mo}(\text{CO})_6$ (6 mol%), PPh_3 (26 mol%), NaHCO_3 (110 mol%), C_6H_6 , 80°, 24 h		(75)		197															
		PhSiH_3 (190 mol%), $\text{Mo}(\text{CO})_6$ (5 mol%), PPh_3 (17 mol%), NaHCO_3 (100 mol%), THF , 65°, 5.5 h		(75)		197															
		PhSiH_3 (200 mol%), $\text{Mo}(\text{CO})_6$ (5 mol%), PPh_3 (23 mol%), NaHCO_3 (100 mol%), THF , 65°, 1.33 h		(80)		197															
	I	Et_3SiH (1.4 eq), PdCl_2 (5-10 mol%), rt, 1 h		(>95)		195															
	I (>95)	Et_3SiH (1.4 eq), PdCl_2 (5-10 mol%), rt, 40 min	I			195															

TABLE 4. ORGANOSILANE REDUCTION OF HALOCARBONS (Continued)

Halocarbon	Conditions	Product(s) and Yield(s) (%)				Refs.
C ₆₋₁₂ 	PMHS, (Ph ₃ P) ₄ Pd (5 mol%), MeCN, DMSO, Br ₃ N (1.4 eq)	R	X	Temp	Time	
		H	I	60°	3 h	(53) 199
		H	Br	110°	18 h	(75) 199
		H	Cl	110°	18 h	NR
		4-Cl	Br	110°	18 h	(65)
		4-Ac	Br	110°	3 h	(96)
		4-O ₂ N	Br	110°	3 h	(93)
		4-BzC ₆ H ₄	Br	110°	5 h	(72)
		4-CHO	Br	110°	3 h	(93)
		4-CO ₂ H	Br	110°	18 h	(77)
C ₇ 	Et ₃ SiH (5 eq), AlCl ₃ (0.1 eq), HCl		(73)			146
	Et ₃ SiH (12 eq), AlCl ₃ (0.4 eq), C ₃ H ₁₂ , 40°, <1 h	I (64)				186
	Et ₃ SiH (2.5 eq), AlCl ₃ (0.25 eq), 20°, 30 min	I (76) + 	II (11) + 			189
	Et ₃ SiH (6 eq), AlCl ₃ (0.55 eq), 20°, 30 min	I (83) + II (3) + III (3)			III (7)	189
	Et ₃ SiH (6 eq), AlCl ₃ (0.55 eq), 20°, 30 min	I (76)				189
	R ₃ SiH (1.3 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%), R ₃ = Et ₃ , EtMe ₂ , Ph ₂ Et, (C ₆ H ₁₁) ₂ Et		(90+95)			188

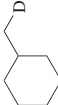



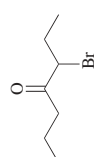
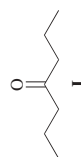
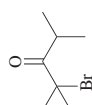
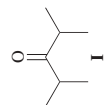

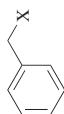
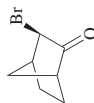
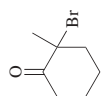
	Et ₃ SiD (1.4 eq), PdCl ₂ (5-10 mol%), rt	195
I (52)	Et ₃ SiH (12 eq), AlCl ₃ (0.4 eq), C ₅ H ₁₂ , 40°, <1 h	186
	Et ₃ SiD (12 eq), AlCl ₃ (0.4 eq), C ₅ H ₁₂ , 40°, <1 h	186
I	R ₃ Si (x eq), AlCl ₃ (y eq), CH ₂ Cl ₂ , 18-20°, 15 min	187
I (92)	EtCl ₂ SiH (2 eq), AlBr ₃ (0.25 eq), 20°, 2 h	192
I (93-96)	R ₃ SiH (1.3 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%) R ₃ = Et ₃ , <i>n</i> -BuH ₂ , Ph ₂ H, (<i>c</i> -C ₆ H ₁₁) ₂ Et	188
I (87)	Et ₃ SiH (2.5 eq), AlCl ₃ (0.25 eq), 20°, 30 min	189
	Et ₃ SiH (1.3 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%)	188
I (—)	Et ₃ SiH (1.4 eq), PdCl ₂ (5-10 mol%), rt	195
	R ₃ SiH (1.3 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%) R ₃ = Et ₃ , <i>n</i> -BuH ₂ , Ph ₂ H, (<i>c</i> -C ₆ H ₁₁) ₂ Et	188
II	Et ₃ SiH (5 eq), AlCl ₃ (0.1 eq), HCl	146
I (1) + II (65)	<i>n</i> -BuSiH ₃ (5 eq), AlCl ₃ (0.1 eq), HCl	146

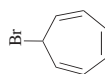
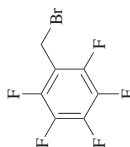


TABLE 4. ORGANOSILANE REDUCTION OF HALOCARBONS (Continued)

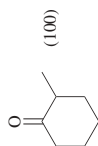
Halocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
	Ph_2SiH_2 (1.1 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (7 mol%), ZnCl_2 (0.33 eq), THF, rt, 12 h	 I (50)	197																																																
	Ph_2SiH_2 (1.4 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (8 mol%), rt, THF, 24 h	I (60)	197																																																
	Ph_2SiH_2 (0.9 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (3.5 mol%), NaOAc (1.6 eq), THF, rt, 4 h	I (60)	197																																																
	Ph_2SiH_2 (1.1 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (7 mol%), K_2CO_3 (1.0 eq), THF, rt, 6 h	I (70)	197																																																
	PhSiH_3 (w mol%), Mo(CO)_6 (x mol%), PPh_3 (y mol%), NaHCO_3 (z mol%)	I	197																																																
	<table><tr><th>w</th><th>x</th><th>y</th><th>z</th><th>Solvent</th><th>Temp</th><th>Time</th><th>I</th></tr><tr><td>200</td><td>20</td><td>0</td><td>0</td><td>THF</td><td>65°</td><td>4.0 h</td><td>(75)</td></tr><tr><td>180</td><td>49</td><td>0</td><td>0</td><td>THF</td><td>65°</td><td>2.5 h</td><td>(100)</td></tr><tr><td>230</td><td>23</td><td>0</td><td>260</td><td>THF</td><td>65°</td><td>1.75 h</td><td>(100)</td></tr><tr><td>150</td><td>5</td><td>17</td><td>100</td><td>THF</td><td>65°</td><td>2.25 h</td><td>(100)</td></tr><tr><td>150</td><td>6</td><td>23</td><td>110</td><td>C_6H_6</td><td>80°</td><td>2.75 h</td><td>(97)</td></tr></table>	w	x	y	z	Solvent	Temp	Time	I	200	20	0	0	THF	65°	4.0 h	(75)	180	49	0	0	THF	65°	2.5 h	(100)	230	23	0	260	THF	65°	1.75 h	(100)	150	5	17	100	THF	65°	2.25 h	(100)	150	6	23	110	C_6H_6	80°	2.75 h	(97)		
w	x	y	z	Solvent	Temp	Time	I																																												
200	20	0	0	THF	65°	4.0 h	(75)																																												
180	49	0	0	THF	65°	2.5 h	(100)																																												
230	23	0	260	THF	65°	1.75 h	(100)																																												
150	5	17	100	THF	65°	2.25 h	(100)																																												
150	6	23	110	C_6H_6	80°	2.75 h	(97)																																												
	Ph_2SiH_2 (3 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (10 mol%), K_2CO_3 (1.8 eq), THF, rt, 12 h	 I (25)	197																																																
	PhSiH_3 (190 mol%), Mo(CO)_6 (5 mol%), PPh_3 (19 mol%), NaHCO_3 (110 mol%), C_6H_6 , 80°, 2.5 h	I (70)	197																																																
	Et_3SiH (12 eq), AlCl_3 (0.4 eq), C_5H_{12} , 40°, <1 h	 I (96)	186																																																
	Et_3SiH (5 eq), AlCl_3 (0.1 eq), HCl	I (96)	146																																																



X = Cl, Br

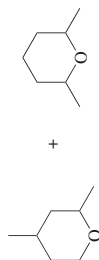


PhSiH₃ (150 mol%), Mo(CO)₆ (6 mol%),
PPh₃ (20 mol%), NaHCO₃ (80 mol%),
THF, 65°, 1.0 h



197

Et₃SiH (3 eq), AlCl₃ (x eq),
HCl, CH₂Cl₂, rt



136

x	Time
0.75	20 h
2	1.5 h



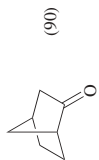
(28)

(30)

(6)

(28)

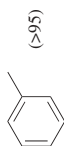
PhSiH₃ (160 mol%), Mo(CO)₆ (6 mol%),
PPh₃ (26 mol%), NaHCO₃ (80 mol%),
MeC₆H₅, 75°, 5.5 h



(90)

197

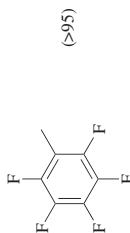
Et₃SiH (1.4 eq), PdCl₂ (5-10 mol%),
rt, 2 min



(>95)

195

Et₃SiH (1.4 eq), PdCl₂ (5-10 mol%),
rt, 2 min



(>95)

195

R₃SiH (x eq), AlCl₃ (0.25 eq),
CH₂Cl₂, 18 to 20°



187

R ₃ Si	x	y	Time
Et ₃ Si	1.5	0.25	30 min
H(SiPh ₂) ₂ Si	0.6	0.6	1 h

(80)

(46)

TABLE 4. ORGANOSILANE REDUCTION OF HALOCARBONS (Continued)

Halocarbon		Conditions	Product(s) and Yield(s) (%)			Refs.
C ₇		Et ₃ SiH (1.4 eq), PdCl ₂ (5-10 mol%), rt, 2 min		(>95)	X 2-Br 2 min 2-I 10 min 4-I 25 min	195
C ₇₋₁₉	RX	[HSi(OEt) ₃] ₄ K, THF	RH + RR			288
	R	Temp Time	I	II		
	<i>n</i> -C ₁₂ H ₂₅	45° 48 h	(33)	(—)		
	<i>n</i> -C ₁₂ H ₂₅	rt 15 h	(47)	(—)		
	Bn	rt 40 h	(16)	(14)		
	Bn	rt 20 h	(37)	(34)		
	Ph ₂ CH	rt 15 h	(12)	(40)		
	Ph ₃ C	rt 15 h	(47)	(22)		
C ₇₋₁₁	ArOTf	Et ₃ SiH (x eq), Pd(OAc) ₂ , ligand, DMF	ArH			201
	Ar	x Ligand Temp Time				
	4-O ₂ NC ₆ H ₄	2.5 dppp 100° 7 d	(67)			
	4-O ₂ NC ₆ H ₄	2.5 dppf 60° 20 min	(100)			
	4-BrC ₆ H ₄	2.5 dppp 43° 1 h	(90)			
	4-(OHC)C ₆ H ₄	2.5 dppp 60° 1 h	(99)			
	4-MeO ₂ CC ₆ H ₄	2.5 dppp 60° 14 h	(100)			
	1-C ₁₀ H ₇	2.5 dppp 60° 5 h	(100)			
	2-(CF ₃ SO ₃)-4- <i>t</i> -BuC ₆ H ₃	5 dppp 60° 22 h	(>99)			
C ₈		R ₃ SiH (1.3 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%)				188
		R ₃ Si				
		Et ₃ Si	(85-90)			
		Et ₂ MeSi	(85-90)			
		Ph ₂ EtSi	(7-8)			
		(<i>c</i> -C ₆ H ₁₁) ₂ EtSi	(7-8)			


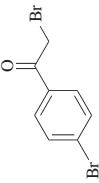
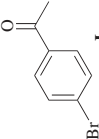
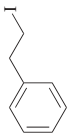
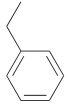
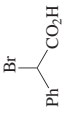



	R_3SiH (1.2–1.5 eq), CH_2Cl_2 , $AlCl_3$ (25 mol%), $R_3Si = Et_3Si, Et_2MeSi, n-BuH_2Si,$ $Ph_2HSi, Ph_3Si, (C_6H_{11})_2EtSi$		(80–95)	188
	$PhSiH_3$ (140 mol%), $Mo(CO)_6$ (4 mol%), PPh_3 (18 mol%), $NaHCO_3$ (70 mol%), THF, 65°, 4.5 h	 I	(90)	197
	Ph_2SiH_2 (1.3 eq), $ZnCl_2$ (2.8 eq), $(Ph_3P)_4Pd$ (7 mol%), $CHCl_3$, rt, 1 h	I (70)		197
	Ph_2SiH_2 (1.5 eq), $(Ph_3P)_4Pd$ (8 mol%), THF, rt, 0.5 h	I (73)		197
	Et_3SiH (1.5 eq), $(Ph_3P)_4Pd$ (8 mol%), THF, rt, 20 h	I (5)		197
	$PhSiH_3$ (1.5 eq), $(Ph_3P)_4Pd$ (8 mol%), THF, rt, 0.1 h	I (60)		197
	Ph_2SiH_2 (1.4 eq), $Pd(OAc)_2$ (8 mol%), PPh_3 (0.16 eq), THF, rt, 24 h	I (70)		197
	$PhSiH_3$ (120 mol%), $Mo(CO)_6$ (6 mol%), PPh_3 (27 mol%), $NaHCO_3$ (110 mol%), C_6H_6 , 80°, 3.25 h	I (95)		197
	$PMHS, (Ph_3P)_4Pd$ (5 mol%), MeCN, DMSO, Bn_3N (1.4 eq), 110°, 3 h	I (80)		199

TABLE 4. ORGANOSILANE REDUCTION OF HALOCARBONS (Continued)

Halocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>PhSiH₃ (210 mol%), Mo(CO)₆ (5 mol%), PPh₃ (20 mol%), NaHCO₃ (150 mol%), THF, 65°, 4.5 h</p>	 <p>I (100)</p>	197
	<p>PhSiH₃ (150 mol%), Mo(CO)₆ (8 mol%), PPh₃ (33 mol%), NaHCO₃ (130 mol%), C₆H₆, 80°, 2.0 h</p>	<p>I (>95)</p>	197
	<p>PhSiH₃ (200 mol%), Mo(CO)₆ (5 mol%), PPh₃ (19 mol%), NaHCO₃ (140 mol%), MeC₆H₅, 95°, 1.0 h</p>	<p>I (>95)</p>	197
	<p>Et₃SiH (1.4 eq), PdCl₂ (5-10 mol%), rt, 10 min</p>	 <p>(>95)</p>	195
	<p>PMHS, (Ph₃P)₄Pd (5 mol %), MeCN, DMSO, Bn₃N (1.4 eq), 110°, 18 h</p>	 <p>(55)</p>	199
	<p>PMHS, (Ph₃P)₄Pd (5 mol %), MeCN, DMSO, Bn₃N (1.4 eq), 60°, 3 h</p>	 <p>(37)</p>	199

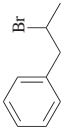
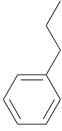
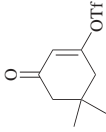
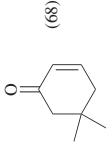
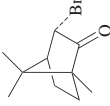
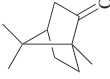






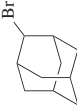

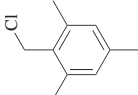
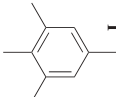

C ₉			Et ₃ SiH (12 eq), AlCl ₃ (0.4 eq), C ₃ H ₁₂ , 40°, <1 h	(43)	186
			Et ₃ SiH (5 eq), AlCl ₃ (0.1 eq), HCl	I (43)	
			Et ₃ SiH (2.5 eq), Pd(OAc) ₂ , dppp, Et ₃ N (2 eq), DMF, rt, 40 min	(68)	146, 201
C ₁₀			PhSiH ₃ (160 mol%), Mo(CO) ₆ (11 mol%), THF, 65°, 2.5 h	(100)	197
			PhSiH ₃ (280 mol%), Mo(CO) ₆ (65 mol%), PPh ₃ (24 mol%), NaHCO ₃ (130 mol%), MeC ₆ H ₅ , 75°, 12.0 h	I (45)	197
			Ph ₂ SiH ₂ (3 eq), (Ph ₃ P) ₄ Pd (10 mol%), K ₂ CO ₃ (1.8 eq), THF, rt, 12 h	I (55)	197
			Et ₃ SiH (1.3 eq), AlCl ₃ (0.25 eq), CH ₂ Cl ₂ , 18-20°, 15 min	(88)	187
			H(Ph ₃ Si) ₄ H (0.6 eq), AlCl ₃ (0.25 eq), CH ₂ Cl ₂ , 18-20°, 15 min	I (88)	187
			Et ₃ SiH (1.4 eq), PdCl ₂ (5-10 mol%), 80°, 4 h	I (84)	195

TABLE 4. ORGANOSILANE REDUCTION OF HALOCARBONS (Continued)

Halocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₀	Et ₃ SiH (5 eq), AlCl ₃ (0.1 eq), HCl	 I (84)	146
	R ₃ SiH (1.3–1.5 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%) R ₃ Si = Et ₃ Si, Et ₂ MeSi, Ph ₂ HSi, (c-C ₆ H ₁₁) ₂ EtSi	I (90–96)	188
	Et ₃ SiH (12 eq), AlCl ₃ (0.4 eq), C ₃ H ₁₂ , 40°, <1 h	I (79)	186
	Et ₃ SiH (12 eq), AlCl ₃ (0.4 eq), C ₃ H ₁₂ , 40°, <1 h	I (84)	186
	Et ₃ SiH (1.4 eq), PdCl ₂ (5–10 mol%), 80°, 6 h	I (80)	195
	Et ₃ SiH (1.4 eq), PdCl ₂ (5–10 mol%), rt, 2 h	I (78)	195
	Et ₃ SiH (1.46 eq), TFA (3 eq), CH ₂ Cl ₂ , rt, 2.5 h	 I (79) +  (9)	128
	Et ₃ SiH (1.5 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%)	I (80)	188
	Ph ₂ EtSiH (1.5 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%)	I (45)	188
	(c-C ₆ H ₁₁) ₂ EtSi (1.5 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%)	I (35)	188

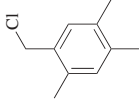
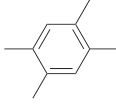
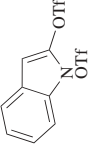
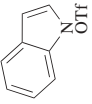
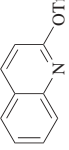
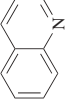
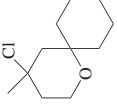
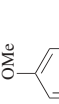
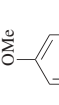
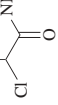
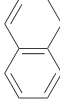


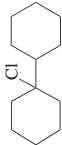
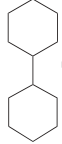


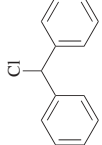
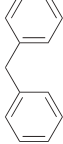
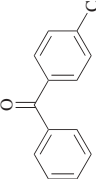
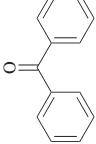
C ₁₀		R_3SiH (x eq), $AlCl_3$ (0.25 eq), CH_2Cl_2 , 18-20°, 1 h		187
		$\frac{R_3SiH}{Et_3SiH} \times \frac{1.3}{1.3}$ $\frac{H(SiPh_2)_4H}{H(SiPh_2)_4H} \frac{0.6}{0.6}$	(78) (56)	
		Et_3SiH (2.5 eq), $Pd(OAc)_2$, dppp, DMF, rt, 10 h		201
		Et_3SiH (2.5 eq), $Pd(OAc)_2$, dppp, DMF, 60°, 4 h		201
C ₁₁		Et_3SiH (3 eq), $AlCl_3$ (1 eq), HCl , CH_2Cl_2 , rt, 1 h		136
		Et_3SiH (1.5 eq), TFA (5 eq), CH_2Cl_2 , rt, 18 h	(54)	198
		Et_3SiH (2.5 eq), $Pd(OAc)_2$, dppp, DMF, 60°, 4 h		201
C ₁₂		n -Bu SiH_3 (5 eq), $AlCl_3$ (0.1 eq), HCl		146
			(82)	

TABLE 4. ORGANOSILANE REDUCTION OF HALOCARBONS (Continued)

Halocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂ 	Et ₃ SiH (1.3 eq), AlCl ₃ (0.25 eq), CH ₂ Cl ₂ , 18-20°, 15 min	 I (95)	187
C ₁₃ 	H(Ph ₂ Si) ₄ H (0.6 eq), AlCl ₃ (0.25 eq), CH ₂ Cl ₂ , 18-20°, 15 min	I (96)	187
	<i>n</i> -Bu ₃ SiH ₃ , AlCl ₃ (0.4 eq), C ₃ H ₁₂ , 40°, <1 h	 I (82)	186
	<i>n</i> -Bu ₃ SiH, AlCl ₃ (0.4 eq), C ₃ H ₁₂ , 40°, <1 h	I (87)	186
	Et ₃ SiH (5 eq), AlCl ₃ (0.1 eq), HCl	 I (100)	146
	Et ₃ SiH (12 eq), AlCl ₃ (0.4 eq), C ₃ H ₁₂ , 40°, <1 h	I (100)	186
	Et ₃ SiH (1.5 eq), AlCl ₃ (0.5 eq), CH ₂ Cl ₂ , 18-20°, 15 min	I (95)	187
	H(Ph ₂ Si) ₄ H (0.6 eq), AlCl ₃ (0.5 eq), CH ₂ Cl ₂ , 18-20°, 15 min	I (95)	187
	R ₃ SiH (1.3-1.5 eq), CH ₂ Cl ₂ , AlCl ₃ (25 mol%) R ₃ Si = Et ₃ Si, Et ₂ MeSi, Ph ₂ HSi, (<i>o</i> -C ₆ H ₁₁) ₂ EtSi	I (80-88)	188
	HMe ₂ SiOSiMe ₂ H (2 eq), 10% Ni/C, PPh ₃ (40%), dioxane, reflux, 15 h	 I (96)	200

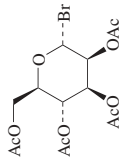
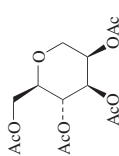
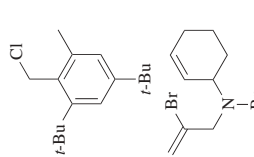
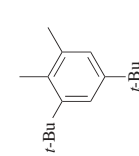
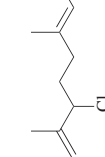
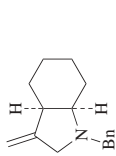


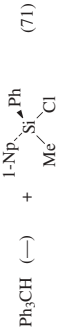
C ₁₄		Et ₃ SiH (1.4 eq), PdCl ₂ (5-10 mol%), rt, 40 min		195
C ₁₆		Et ₃ SiH (2 eq), TFA (2 eq), CH ₂ Cl ₂ , 40°, 40 min, rt, 15 h		128
C ₁₇		1. Ni(cod) ₂ (1.23 eq), Et ₃ N (3 eq), MeCN 2. Et ₃ SiH (4 eq)		706, 705
C ₁₉		Ph ₂ SiH ₂ (2.9 eq), ZnCl ₂ (3-4 eq), (Ph ₃ P) ₄ Pd (5.0 mol%), THF, rt, 12 h; 50° 6 h		196
		1-Np-Si(Ph)(Me)H + 1-Np-Si(Ph)(Me)Cl		60
		R ₃ SiH, rt	Ph ₃ CH	59
	X	R ₃ Si	Solvent	Time
	Cl	Ph ₃ Si	CH ₂ Cl ₂	10 min
	Cl	Ph ₃ Si	C ₆ H ₆	24 h
	Cl	Et ₃ Si	CH ₂ Cl ₂	10 min
	Br	Ph ₃ Si	CH ₂ Cl ₂	10 min
	Br	Ph ₃ Si	C ₆ H ₆	24 h
	Br	Et ₃ Si	CH ₂ Cl ₂	10 min

TABLE 4. ORGANOSILANE REDUCTION OF HALOCARBONS (Continued)

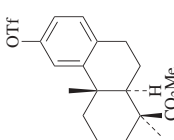
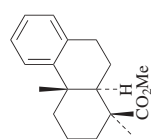
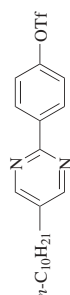
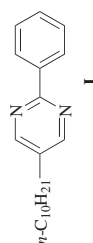
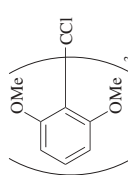
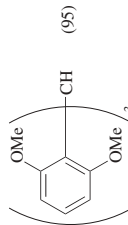
Halocarbon	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₉ 	Et ₃ SiH (3 eq), Pd(OAc) ₂ , dppp, DMF, 60°, 22 h	(92) 	201
C ₂₁ 	Et ₃ SiH (2.5 eq), Pd(OAc) ₂ , dppp, DMF, 60°, 4 h	(99) 	201
	Et ₃ SiH (2.5 eq), Pd(OAc) ₂ , dppp, DMF, 80°, 9 d	I (41)	201
	Et ₃ SiH (2.5 eq), Pd(OAc) ₂ , dpp, DMF, 60°, 10 min	I (100)	201
C ₂₅ 	Et ₃ SiH (4 eq), HOAc, rt, 1 h	(95) 	29

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS

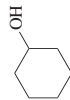


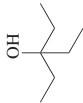


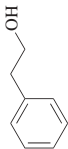
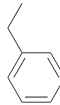
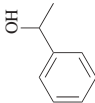
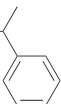
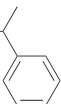
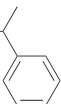
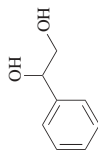
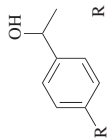
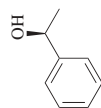
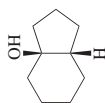
Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	Et ₃ SiH (4 eq), AlCl ₃ (1.5 eq), HCl, CH ₂ Cl ₂ , rt, 3.5 h	 I (70) +  II (7)	136
C ₆ -C ₁₀ R-OH	Et ₃ SiH (4 eq), AlCl ₃ (1.5 eq), CH ₂ Cl ₂ , rt, 3.5 h	I (53) + II (6)	136
	Et ₃ SiH (x eq), (C ₆ F ₅) ₃ B (10 mol %), C ₆ H ₁₄ or CH ₂ Cl ₂ , rt, 20 h	R-H I + ROSiEt ₃ II	144
R	x	I II	
<i>c</i> -C ₆ H ₁₁	6.0	(—) (>95)	
Ph	1.1	(0) (>99)	
<i>c</i> -C ₆ H ₁₁ CH ₂	6.0	(91) (—)	
Ph(Me)CH	6.0	(—) (>95)	
BnCH ₂	3.0	(>95) (—)	
<i>n</i> -C ₉ H ₁₉	1.1	(—) (>95)	
<i>n</i> -C ₉ H ₁₉	3.0	(>99) (0)	
Bn(CH ₂) ₂	3.0	(>95) (—)	
2-C ₉ H ₁₇	3.0	(—) (>95)	
Bn(Me) ₂ C	3.0	(—) (86)	

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.																	
	Ph ₃ SiH (1.2 eq), TFA (6.5 eq), CH ₂ Cl ₂ , rt, 24 h	 (78)	127																	
	Et ₃ SiH (2 eq), AlCl ₃ (1.1 eq), HCl, CH ₂ Cl ₂ , rt, 45 min	 (91)	136																	
	Et ₃ SiH (3 eq), AlCl ₃ (1.5 eq), CH ₂ Cl ₂ , rt	I (94)	136																	
	Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (5 mol %), C ₆ H ₁₄ or CH ₂ Cl ₂ , rt, 20 h	 (>95)	145																	
	Et ₃ SiH (1 eq), acid, rt, 96 h	I	134																	
	Et ₃ SiH (x mol%), TFA (y mol%), 50°, 15 h	<table><tr><th colspan="2">Acid</th></tr><tr><th>Solvent</th><th>x y</th></tr><tr><td>CHCl₃</td><td>0.5 9 (94)</td></tr><tr><td>4-O₂NC₆H₅</td><td>0.2 12 (56)</td></tr></table>	Acid		Solvent	x y	CHCl ₃	0.5 9 (94)	4-O ₂ NC ₆ H ₅	0.2 12 (56)	134									
Acid																				
Solvent	x y																			
CHCl ₃	0.5 9 (94)																			
4-O ₂ NC ₆ H ₅	0.2 12 (56)																			
	Ph ₂ ClSiH (2 eq), InCl ₃ (0.05 eq), CH ₂ Cl ₂ , rt, 1 h	I (88)	172																	
	Et ₃ SiH (x eq), Et ₃ SiD (x eq), CH ₂ Cl ₂ , 0°, 0.5 h	<table><tr><th rowspan="2">I + </th><th colspan="2">k_H/k_D</th></tr><tr><th>x</th><th></th></tr><tr><td></td><td>1.67</td><td>1.05</td></tr><tr><td></td><td>1.0</td><td>0.99</td></tr><tr><td></td><td>0.71</td><td>1.01</td></tr><tr><td></td><td>0.5</td><td>0.98</td></tr></table>	I + 	k _H /k _D		x			1.67	1.05		1.0	0.99		0.71	1.01		0.5	0.98	133
	I + 	k _H /k _D																		
x																				
	1.67	1.05																		
	1.0	0.99																		
	0.71	1.01																		
	0.5	0.98																		



C₉



Et₃SiH, CH₂Cl₂, 0°, 0.5 h

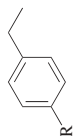
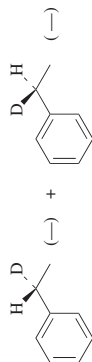
Ph₂ClSiH (2 eq), InCl₃ (0.05 eq)

Solvent	Temp	Time
CH ₂ Cl ₂	rt	2 h
ClCH ₂ CH ₂ Cl	80°	3 h
ClCH ₂ CH ₂ Cl	80°	3 h

Et₃SiH (2 eq), BF₃•OEt₂ (2 eq),
CH₂Cl₂, rt, 20 h

Ph(*n*-BuCH₂)MeSiH (2-10 mol%),
BF₃, CH₂Cl₂, rt, 10 min

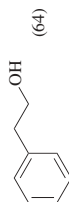
Ph₃SiH, TFA, CH₂Cl₂



(70)

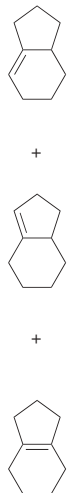
(83)

(95)



(64)

(50)



III

V

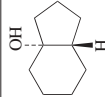





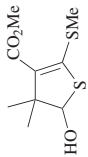

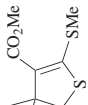

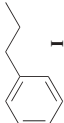
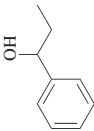
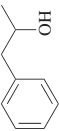
IV

I + II + III + IV + V (100), I:II:III:IV:V = 95:5:0:0:0

I + II + III + IV + V (100), I:II:III:IV:V = 83:7:0:6:4

Et₃SiH, TFA, CH₂Cl₂

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)		Refs.
 C ₉	Ph ₃ SiH, TFA, CH ₂ Cl ₂	 +  +  131		
		 +  I + II + III + IV + V (100), I:II:III:IV:V = 90:6:3:0:1 I + II + III + IV + V (100), I:II:III:IV:V = 62:13:7:3:15 131		
 	Et ₃ SiH, BF ₃ •OEt ₂ , CH ₂ Cl ₂ , 0°, 1 hr, 20°, 3 h	 (36) +  (—) 708		
	Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (5 mol%), C ₆ H ₁₄ or CH ₂ Cl ₂ , rt, 20 h	 I (>95) 145		
	Ph ₂ ClSiH (2 eq), InCl ₃ (5 mol%), ClCH ₂ CH ₂ Cl, 80°, 5 h	I (0)		172
	Ph ₂ ClSiH (2 eq), InCl ₃ (5 mol%), CH ₂ Cl ₂ , rt, 1 h	I (90)		172
	Ph ₂ ClSiH (2 eq), InCl ₃ (5 mol%), ClCH ₂ CH ₂ Cl, 80°, 6 h	I (54)		172

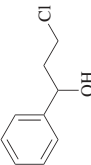

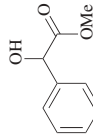
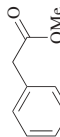

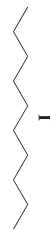


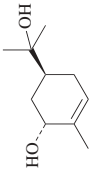
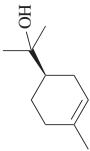
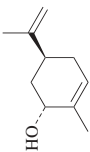
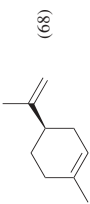
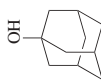

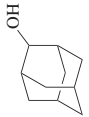

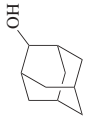


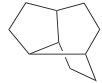
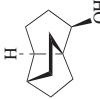
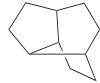
	$\text{Ph}_2\text{C(Si)H}$ (2 eq), InCl_3 (0.05 eq), $\text{ClCH}_2\text{CH}_2\text{Cl}$, 80° , 0.5 h		(95)	172
	Et_3SiH (2 eq), $\text{BF}_3\cdot\text{OEt}_2$ (2 eq), CH_2Cl_2 , 0° , 30 min		(0)	133
	R_3SiH (2 eq), catalyst (5 mol%), 4 h		I	172
	R_3Si	Catalyst	Solvent	Temp
	$\text{Ph}_2\text{C(Si)}$	InCl_3	DCE	80° (76)
	$\text{Ph}_2\text{C(Si)}$	none	DCE	80° (5)
	$\text{Ph}_2\text{C(Si)}$	AlCl_3	DCE	80° (23)
	$\text{Ph}_2\text{C(Si)}$	$\text{BF}_3\cdot\text{OEt}_2$	DCE	80° (tr)
	Ph_2HSi	InCl_3	DCE	80° (19)
	Et_3Si	InCl_3	DCE	80° (0)
	$\text{Me}_2\text{C(Si)}$	InCl_3	DCE	rt (0)
	$\text{Ph}_2\text{C(Si)}$	InCl_3	C_6H_{14}	70° (33)
	$\text{Ph}_2\text{C(Si)}$	InCl_3	C_6H_6	80° (20)
	$\text{Ph}_2\text{C(Si)}$	InCl_3	THF	63° (0)
	$\text{Ph}_2\text{C(Si)}$	InCl_3	MeCN	80° (0)
	$\text{Ph}_2\text{C(Si)H}$ (2 eq), InCl_3 (0.05 eq), $\text{ClCH}_2\text{CH}_2\text{Cl}$, 80° , 4 h		I (76)	172
	$\text{Ph}_2\text{C(Si)H}$ (2 eq), InCl_3 (0.05 eq), $\text{ClCH}_2\text{CH}_2\text{Cl}$, 80° , 4 h		I (74)	172

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Et_3SiH (3 eq), $LiClO_4$, Et_2O , rt, 16 h	 (52)	173
	Et_3SiH (3 eq), $LiClO_4$, Et_2O , rt, 16 h	 (68)	173
	Et_3SiH (1.3 eq), NH_4F (1.3 eq), TFA (5 eq), 0° , 0.5 h; rt, 3 h	 I (97)	135
	Ph_2ClSiH (2 eq), $InCl_3$ (0.05 eq), CH_2Cl_2 , 80° , 3 h	 I (99)	126, 172
	Et_3SiH (3.3 eq), BF_3 , CH_2Cl_2 , rt, 30 min	 I (86)	126
	Et_3SiH , BF_3 , CH_2Cl_2 , rt, 30 min	 (100)	132
	Et_3SiH , BF_3 , CH_2Cl_2 , rt, 30 min	 (100)	132





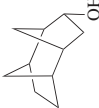
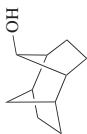

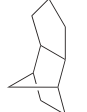





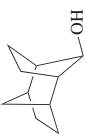


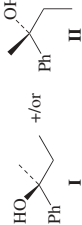


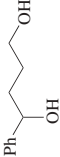

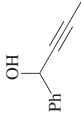

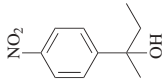
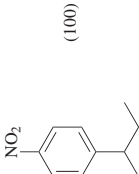
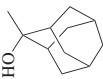

	$\text{Et}_3\text{SiH}, \text{BF}_3, \text{CH}_2\text{Cl}_2, 5-10 \text{ min}$	 I (55-60) +  II (80-85) +  (5)	503
	$\text{Et}_3\text{SiH}, \text{BF}_3, \text{CH}_2\text{Cl}_2, 5-10 \text{ min}$	I (85) + II (<5)	503
	$\text{Et}_3\text{SiH}, \text{BF}_3, \text{CH}_2\text{Cl}_2, 60 \text{ min}$	II (50-55) +  III (10) +  IV (30-35)	503
	$\text{Et}_3\text{SiH}, \text{BF}_3, \text{CH}_2\text{Cl}_2, 5-10 \text{ min}$	II (20-25) + III (5) + IV (40-45) +  V (15-25)	503
	$\text{Et}_3\text{SiH}, \text{BF}_3, \text{CH}_2\text{Cl}_2, 5-10 \text{ min}$	I (95) + II (5)	503
	$\text{Et}_3\text{SiH}, \text{BF}_3, \text{CH}_2\text{Cl}_2, 5-10 \text{ min}$	I (5)	503
	$\text{Et}_3\text{SiH}, \text{BF}_3, \text{CH}_2\text{Cl}_2, 60 \text{ min}$	I (15) + II (<5)	503
	$\text{Et}_3\text{SiH}, \text{BF}_3, \text{CH}_2\text{Cl}_2, 5-10 \text{ min}$	II (40-45) + IV (40) +  VI (15-20)	503
	$\text{Et}_3\text{SiH}, \text{BF}_3, \text{CH}_2\text{Cl}_2, 5-10 \text{ min}$	II (35-40) + IV (35-40) + VI (20-25)	503

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₀</p>  <p>I</p> <p>+ / or</p>  <p>II</p>	<p>R₃SiH (1 eq), TFA, CH₂Cl₂, rt, 20 min</p>		141, 142
<p>Substrate</p> <p>I + II</p>	<p>Silane</p> <p>R₃Si</p> <p>(%) Opt. Purity</p>	<p>Conf.</p>	
II	(R)-1-NpPhMeSi	88.8	(82) R
I	(R)-1-NpPhMeSi	96.2	(81) R
II	(R)-1-NpPhMeSi	96.2	(75) R
II	(S)-1-NpPhMeSi	89.0	(84) S
I	(S)-1-NpPhMeSi	89.0	(75) S
II	Et ₃ Si	—	(85) —
	<p>Ph₂ClSiH (2 eq), InCl₃ (0.05 eq), ClCH₂CH₂Cl, 80°, 3 h</p>	 <p>(53)</p>	172
	<p>Et₃SiH, TFA</p>	 <p>(—)</p>	708
	<p>Ph(<i>t</i>-BuCH₂)MeSiH (2-10 mol%), BF₃, CH₂Cl₂, 0°, 10 min</p>	 <p>(100)</p>	126
<p>C₁₁</p> 	<p>Ph₃SiH (1.1 eq), TFA, CH₂Cl₂, rt</p>	 <p>(41)</p>	127

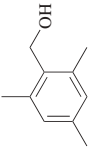
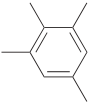
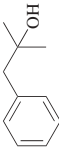
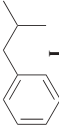
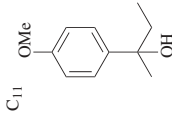
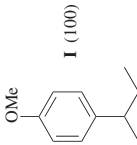
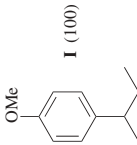
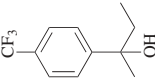
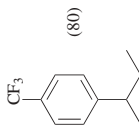
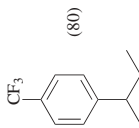
		Ph ₃ SiH (3 eq), TFA, rt, 48 h	(41, 89 ^a)	26								
		Et ₃ SiH (1 eq), acid, rt	I	134								
		<table><tr><th>Acid</th><th>Time</th></tr><tr><td>H₂SO₄·HOAc</td><td>96 h</td></tr><tr><td>4-MeC₆H₄CO₂H/HOAc</td><td>672 h</td></tr><tr><td>TFA</td><td>96 h</td></tr></table>	Acid	Time	H ₂ SO ₄ ·HOAc	96 h	4-MeC ₆ H ₄ CO ₂ H/HOAc	672 h	TFA	96 h	(10) (60) (100)	
Acid	Time											
H ₂ SO ₄ ·HOAc	96 h											
4-MeC ₆ H ₄ CO ₂ H/HOAc	672 h											
TFA	96 h											
		Ph ₂ ClSiH (2 eq), InCl ₃ (5 mol%), ClCH ₂ CH ₂ Cl, 80°, 3 h	I (99)	172								
C ₁₁		Ph(<i>t</i> -BuCH ₂)MeSiH (2-10 mol%), BF ₃ , CH ₂ Cl ₂ , 0°, 2 min	I (100)	126								
		Ph(<i>t</i> -BuCH ₂)MeSiH (2-10 mol%), TFA, CH ₂ Cl ₂ , 0°, 2 min	I (100)	126								
		Ph(<i>t</i> -BuCH ₂)MeSiH (2-10 mol%), BF ₃ , CH ₂ Cl ₂ , 0°, 2 min	(80)	126								

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

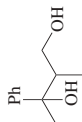
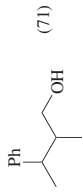
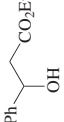

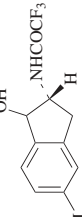
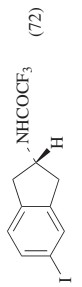
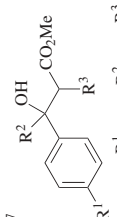
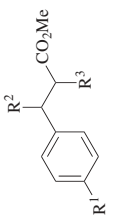
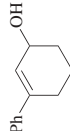
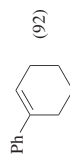




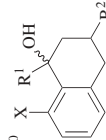

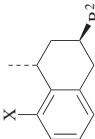
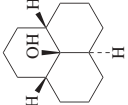
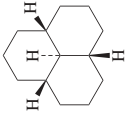



Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 	Et ₃ SiH (2 eq), BF ₃ •OEt ₂ (2 eq), CH ₂ Cl ₂ , 0°, 30 min	 (71)	133
	Ph ₂ ClSiH (2 eq), InCl ₃ (0.05 eq), ClCH ₂ CH ₂ Cl, 80°, 0.5 h	 (68)	172
	Et ₃ SiH, BF ₃ •OEt ₂ , 70°	 (72)	709
C ₁₁₋₁₇ 	Et ₃ SiH (1 eq), BF ₃ •OEt ₂ (1 eq), CH ₂ Cl ₂ , 0°, 1 h		170
		(85)	
		(100)	
		(100)	
		(94)	
		(89)	
		(94)	
C ₁₂ 	Et ₃ SiH (3 eq), LiClO ₄ , Et ₂ O, rt, 16 h	 (92)	173
	Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (5 mol%), C ₆ H ₁₄ or CH ₂ Cl ₂ , rt, 20 h	 (>99)	145
	EtMe ₂ SiH, HBF ₄	 (D)	604

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.												
C_{12-20} 	Et_3SiH (3 eq), TFA (3 eq), CH_2Cl_2 , -78° to 0°	 I +  II <table><tr><th>I + II</th><th>I:II</th></tr><tr><td>(93)</td><td>100:0</td></tr><tr><td>(70)</td><td>100:0</td></tr><tr><td>(86)</td><td>10:1</td></tr><tr><td>(75)</td><td>100:0</td></tr><tr><td>(88)</td><td>100:0</td></tr></table>	I + II	I:II	(93)	100:0	(70)	100:0	(86)	10:1	(75)	100:0	(88)	100:0	162
I + II	I:II														
(93)	100:0														
(70)	100:0														
(86)	10:1														
(75)	100:0														
(88)	100:0														
C_{13} 	Ph_3SiH (1.1 eq), TFA, CH_2Cl_2 , rt, 48 h	 (92)	127												
	R_3SiH (1.2 eq), TFA, CH_2Cl_2 , rt, 30 min	<table><tr><th>R_3Si</th></tr><tr><td>Et_3Si (100)^a</td></tr><tr><td>Ph_3Si (65)</td></tr><tr><td>PhH_2Si (100)^a</td></tr></table>	R_3Si	Et_3Si (100) ^a	Ph_3Si (65)	PhH_2Si (100) ^a	164								
R_3Si															
Et_3Si (100) ^a															
Ph_3Si (65)															
PhH_2Si (100) ^a															
	Et_3SiH (3.0 eq), $(C_6F_5)_3B$ (5 mol%), C_6H_{14} or CH_2Cl_2 , rt, 20 h	 I (98)	145												
	Et_3SiH (1 eq), acid, rt	<table><tr><th>Acid</th><th>Time</th></tr><tr><td>$H_2SO_4/HOAc$</td><td>30 min (60)</td></tr><tr><td>$4-MeC_6H_4CO_2H/HOAc$</td><td>30 min (55)</td></tr><tr><td>TFA</td><td>2 h (70)</td></tr></table>	Acid	Time	$H_2SO_4/HOAc$	30 min (60)	$4-MeC_6H_4CO_2H/HOAc$	30 min (55)	TFA	2 h (70)	134				
Acid	Time														
$H_2SO_4/HOAc$	30 min (60)														
$4-MeC_6H_4CO_2H/HOAc$	30 min (55)														
TFA	2 h (70)														
	Ph_3SiH (3 eq), TFA, rt, 48 h	I (70)	26												
	Ph_2ClSiH (2 eq), $InCl_3$ (0.05 eq), CH_2Cl_2 , rt, 2 h	I (87)	172												

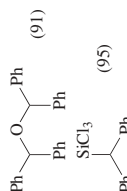
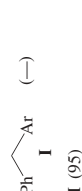
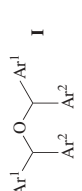



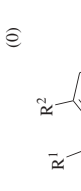
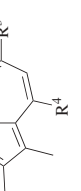


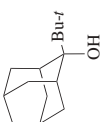

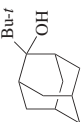
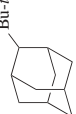
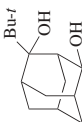
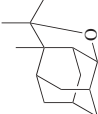
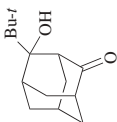

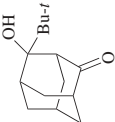

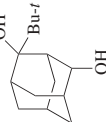

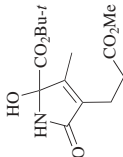
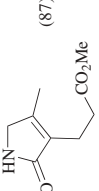
	HMMe ₂ SiOSiMe ₂ H (1.0 eq), TMSOTf (cat.), C ₆ H ₆ , 80°, 240 min		314
	Cl ₃ SiH (3 eq), (<i>n</i> -Pr) ₃ N (1 eq), 55-75°, 1 h		711
	Et ₃ SiH, TFA		712
	Ph ₂ C(SiH) (2 eq), InCl ₃ (5 mol%), CH ₂ Cl ₂ , rt, 3 h		172
	Et ₃ SiH, HOTf, CHCl ₃		713
			
			
			
			
			
			

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{14}	$(n-C_6H_{13})_3SiH$, TFA, CH_2Cl_2 , rt, 10 min	 (90)	151, 152
	Et_3SiH , TFA, CH_2Cl_2 , rt, 16 h	 (82)	153
	Et_3SiH , TFA, CH_2Cl_2 , rt, 16 h	 (81)	153
	Et_3SiH , TFA, CH_2Cl_2 , rt, 16 h	 I (79)	153
	Et_3SiH , TFA, CH_2Cl_2 , rt, 16 h	 I (77)	153
	Et_3SiH , TFA, CH_2Cl_2 , rt, 16 h	 I (78)	153
	Et_3SiH (xs), TFA, 18°, 18 h, 45°, 3 h	 (87)	714

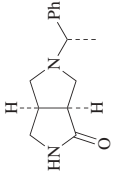
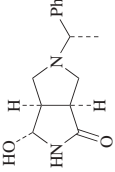
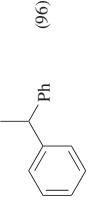
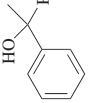
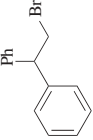
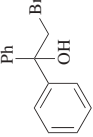
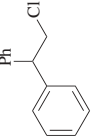
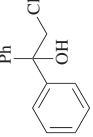
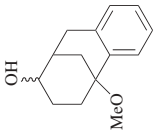
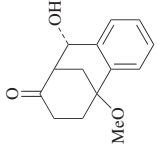
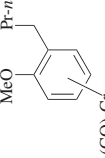
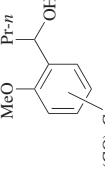
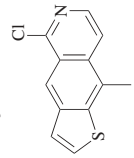
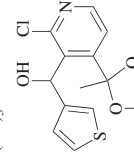
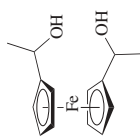
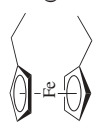
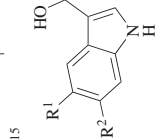
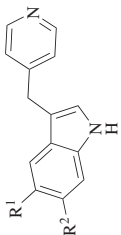
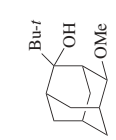
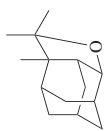
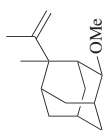
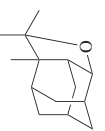
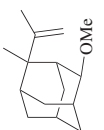
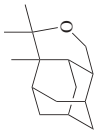
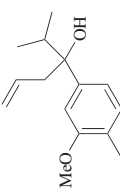
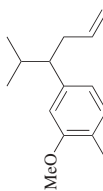
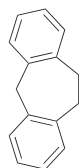
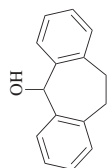
		Et_3SiH , TFA, rt, 16 h	715
		Et_3SiH (1.3 eq), NH_4F (1.3 eq), TFA (5 eq), 0° ; 0.5 h, rt, 4 h	135
		Et_3SiH (1.4 eq), TFA (1 eq), CHCl_3 , 0° , 1 h	184
		Et_3SiH (1.25 eq), TFA (9 eq), CHCl_3 , -15° , 1 h	184
		Et_3SiH , TFA	716
		Et_3SiH , TFA	717
		Et_3SiH (1.1 eq), TFA, rt, 18 h	486

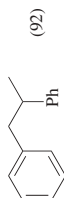
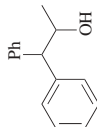
TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.																		
 C ₁₄	Et ₃ SiH (2 eq), TFA, rt, 20 min	 (88)	179																		
 C ₁₄₋₁₅	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt	 R ¹ R ²	718																		
 C ₁₅	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 16 h	<table><tr><th>R¹</th><th>R²</th><th>Time</th></tr><tr><td>H</td><td>H</td><td>16 h (66)</td></tr><tr><td>F</td><td>H</td><td>18 h (80)</td></tr><tr><td>H</td><td>F</td><td>18 h (68)</td></tr><tr><td>NO₂</td><td>H</td><td>2 h (78)</td></tr><tr><td>CN</td><td>H</td><td>4 h (73)</td></tr></table>	R ¹	R ²	Time	H	H	16 h (66)	F	H	18 h (80)	H	F	18 h (68)	NO ₂	H	2 h (78)	CN	H	4 h (73)	153
R ¹	R ²	Time																			
H	H	16 h (66)																			
F	H	18 h (80)																			
H	F	18 h (68)																			
NO ₂	H	2 h (78)																			
CN	H	4 h (73)																			
 (8)	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 16 h	 (53)	153																		
 (8)		 (56)	153																		
 (83)	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 16 h		153																		
	Et ₃ SiH, TFA	 (—)	719																		

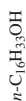


Et₃SiH (1.3 eq), NH₄F (1.3 eq),
TFA (5 eq), 0°, 0.5 h; rt, 4 h

135

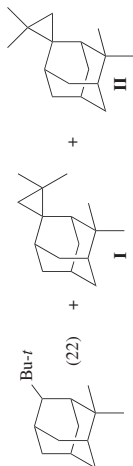
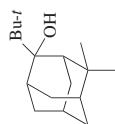

$$\text{Ph}_2\text{ClSiH} \text{ (2 eq), InCl}_3 \text{ (0.05 eq),}$$
$$\text{ClCH}_2\text{CH}_2\text{Cl, 80}^\circ, \text{ 1 h}$$

172

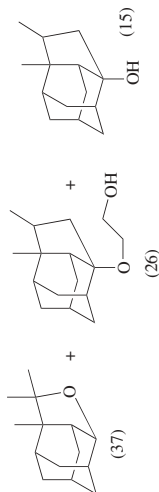
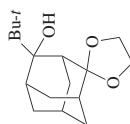
C₁₆

Et_3SiH (3.0 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%),
 C_6H_{14} or CH_2Cl_2 , rt, 20 h

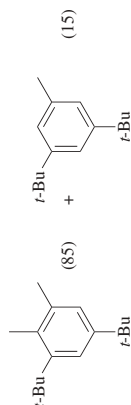
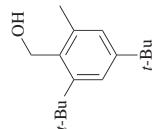
145

 Et_3SiH , TFA, CH_2Cl_2 , rt, 16 h

153

 Et_3SiH , TFA, CH_2Cl_2 , rt, 16 h

153



Et₃SiH (3.1 eq), TFA (6.4 eq),
CH₂Cl₂, rt, 5 h

128

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)					Refs.
	R ₃ SiH (1.3 eq), TFA (2.1 eq), CH ₂ Cl ₂ , rt, 0.5 h		+		+		26
	R ₃ Si	Alcohol	III	IV	V	IV:III	
	Et ₃ Si	I	(20)	(39)	(41)	1.8	
	(<i>n</i> -C ₈ H ₁₇) ₃ Si	I	(15)	(21)	(64)	1.4	
	Ph ₃ Si	I	(10)	(18)	(72)	1.8	
	Et ₃ HSi	I	(12)	(54)	(34)	4.5	
	Ph ₂ HSi	I	(11)	(42)	(47)	3.8	
	PhH ₂ Si	I	(3)	(13)	(84)	4.3	
	Et ₃ Si	II	(28)	(50)	(22)	1.8	
	(<i>n</i> -C ₈ H ₁₇) ₃ Si	II	(24)	(36)	(40)	1.5	
	Ph ₃ Si	II	(20)	(29)	(51)	1.5	
	Ph ₂ HSi	II	(13)	(49)	(38)	3.8	
	Ph ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 0.5 h		+			(84)	24
	Et ₃ SiH, CH ₂ Cl ₂ , 0°, 0.5 h		(-)	+		(-) + HCHO	133
	Et ₃ SiH (2 eq), BF ₃ •OEt ₂ (2 eq), CH ₂ Cl ₂ , -40°, 30 min	I +	+		I + II (92), I:II = >95:5		137

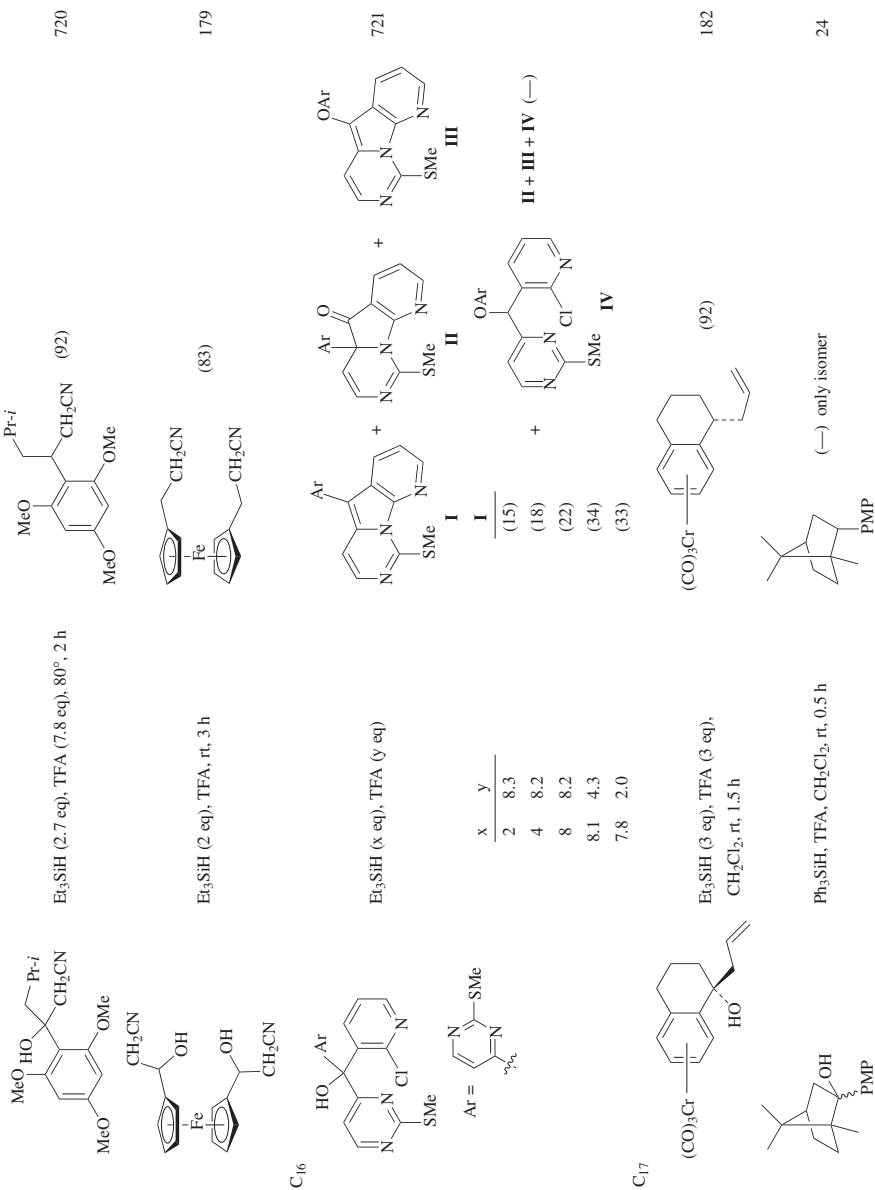
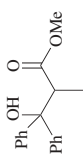
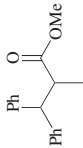
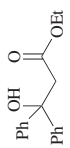
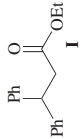
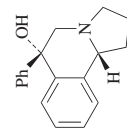
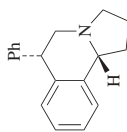
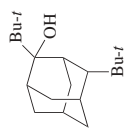
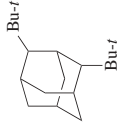
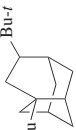
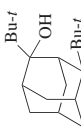
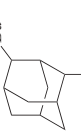
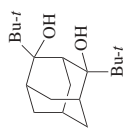
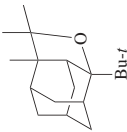


TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₇	Et ₃ SiH (2 eq), BF ₃ •OEt ₂ (2 eq), CH ₂ Cl ₂ , 0°, 30 min	 (89)	137
 C ₁₈	Et ₃ SiH (2 eq), BF ₃ •OEt ₂ (2 eq), CH ₂ Cl ₂ , 0°, 30 min	 I + II (68), I:II = 73:27	137
 C ₁₈	Et ₃ SiH, TFA, 0-5°, 24 h	 (trace)	722
 C ₁₈	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 16 h	 (31) +  (38)	153
 C ₁₈	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 16 h	 (80)	153
 C ₁₈	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 16 h	 (78)	153

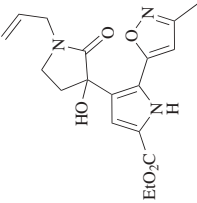
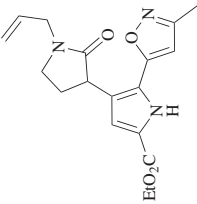
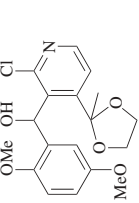
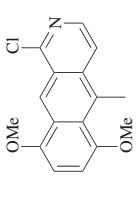
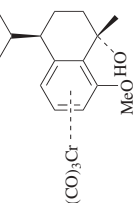
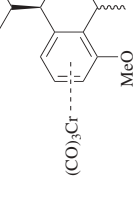
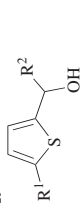
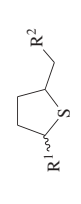
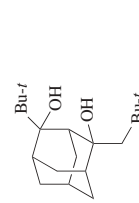
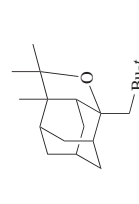
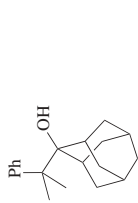
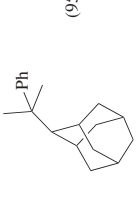
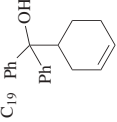
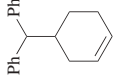
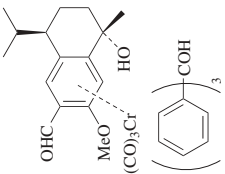
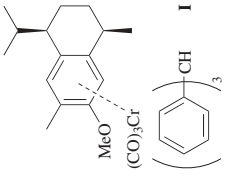
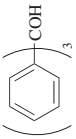
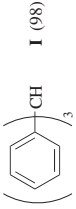


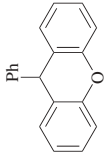

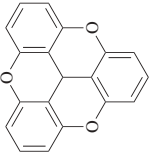
	<p>Et₃SiH (xs), TFA, rt, 2 h</p>		(86)	157
	<p>Et₃SiH (1.1 eq), TFA, rt, 18 h</p>		(65)	486
	<p>Et₃SiH (xs), TFA</p>		(75)	723
<p>C_{18:21}</p> 	<p>Et₃SiH, TFA, 50°, 48 h</p>		<p> $\begin{array}{c} \text{R}^1 \quad \text{R}^2 \\ \hline (-) \quad \text{H} \quad n\text{-C}_{15}\text{H}_{31} \\ \quad \quad \text{H} \quad n\text{-C}_{16}\text{H}_{33} \\ \quad \quad \text{Me} \quad n\text{-C}_{12}\text{H}_{25} \end{array}$ </p>	258
<p>C₁₉</p> 	<p>Et₃SiH, TFA, CH₂Cl₂, rt, 16 h</p>		(81)	153
	<p>Et₃SiH (10 eq), MeSO₃H (1 eq), CH₂Cl₂, -78°, 12 h; 0°, 10 h</p>		(95)	140

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₉	Et ₃ SiH (1 eq), TFA (17 eq), CH ₂ Cl ₂ , rt, 20 h	 (−)	724
	Et ₃ SiH (6 eq), TFA (9 eq), 60°, 4.5 h	 (82)	352, 725
	Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (5 mol%), C ₆ H ₁₄ or CH ₂ Cl ₂ , rt, 20 h	 I (98)	145
	Et ₃ SiH (1 eq), acid, rt, 30 min	 I	134
		Acid H ₂ SO ₄ /HOAc (88) 4-MeC ₆ H ₄ CO ₂ H/HOAc (80) TFA (59)	
	Ph ₃ SiH (3 eq), TFA, rt, 48 h	 I (74)	26
	Et ₃ SiH (3 eq), HOAc, rt, 48 h	 I (95)	26
	Ph ₃ SiH (3 eq), TFA, rt, 48 h	 I (80)	26
	Et ₃ SiH (4 eq), HOAc, reflux, 40 h	 (89)	29

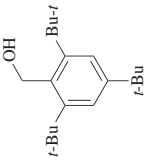
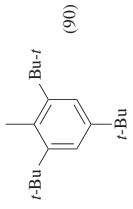
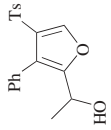
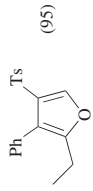
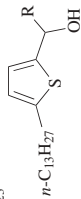
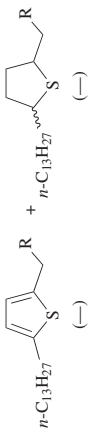
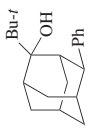
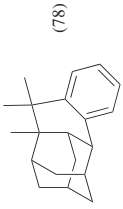
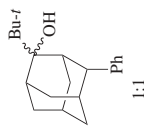
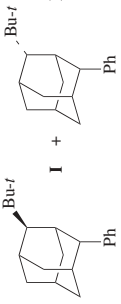
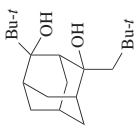
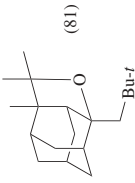
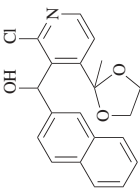
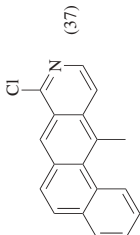
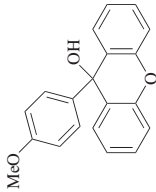
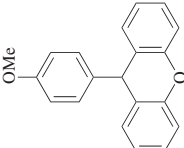
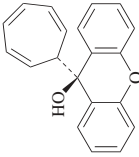

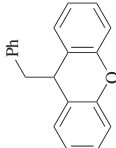
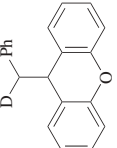
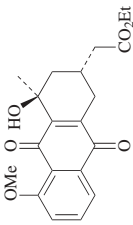
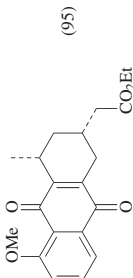
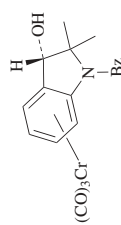
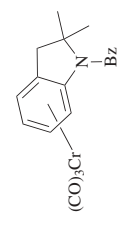
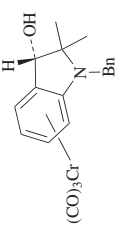
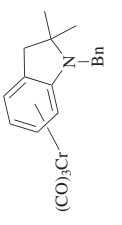
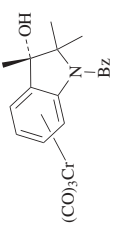
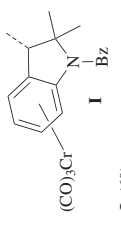
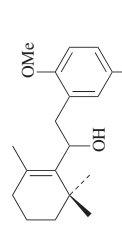
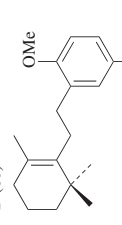
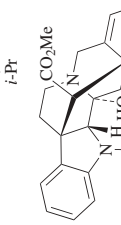
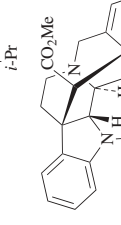
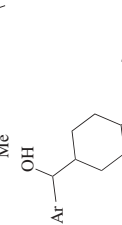
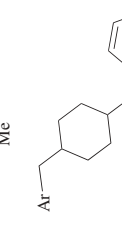
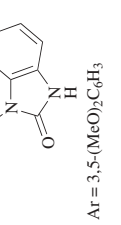
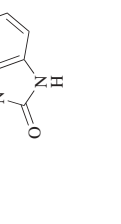
		<p>Et₃SiH (3.2 eq), TFA (5.9 eq), CD₂Cl₂, rt, 1 h</p>	<p>(90)</p> <p>128</p>
		<p>Et₃SiH, TFA, rt</p>	<p>(95)</p> <p>726</p>
<p>C_{19/23}</p> 		<p>Et₃SiH, TFA, 50°, 48 h</p>	<p>258</p>
<p>R = Me, Et, <i>n</i>-Pr, <i>n</i>-Bu, <i>n</i>-C₅H₁₁</p> <p>C₂₀</p> 		<p>Et₃SiH, TFA, CH₂Cl₂, rt, 16 h</p>	<p>(78)</p> <p>153</p>
		<p>Et₃SiH, TFA, CH₂Cl₂, rt, 16 h</p>	<p>I + II (73), I:II = 3:2</p> <p>153</p>
		<p>Et₃SiH, TFA, CH₂Cl₂, rt, 16 h</p>	<p>(81)</p> <p>153</p>

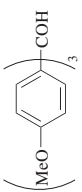
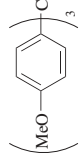
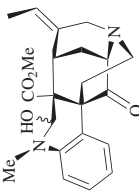
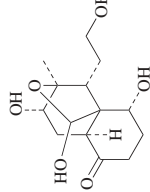
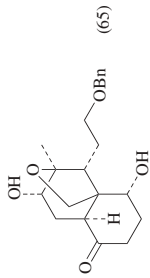
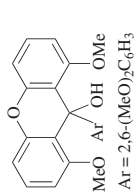
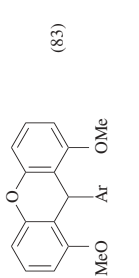
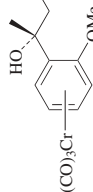
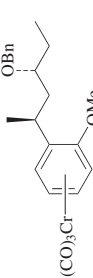
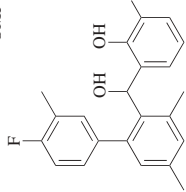
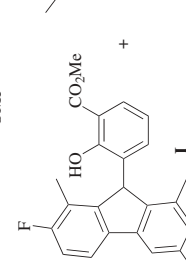
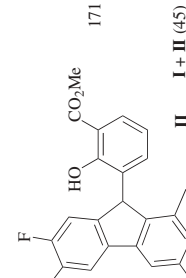
TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₀	Et ₃ SiH (1.1 eq), TFA, rt, 18 h	 (37)	486
	Et ₃ SiH (3 eq), TFA, rt, 48 h	 1 (68)	26
	Ph ₃ SiH (3 eq), TFA, rt, 48 h	 1 (94)	26
	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 15 min	 (88)	64
	Et ₃ SiD, TFA, CH ₂ Cl ₂ , rt, 15 min	 (75)	64
	Et ₃ SiH (3 eq), TFA (3 eq), CH ₂ Cl ₂ , -78° to 0°	 (95)	162

	Et_3SiH , HPF_6 , CH_2Cl_2 , -30° , 1 h		(52)	727
	Et_3SiH , HPF_6 , CH_2Cl_2 , -30° , 0.25 h		(89)	727
C_{21} 	Et_3SiH , HPF_6 , CH_2Cl_2 , -30° , 1 h		(65)	727
	Et_3SiH , TFA, CH_2Cl_2 , rt, 1 h		I (60)	727
	Et_3SiH , $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , -10° , 1 h		(69)	174
	Et_3SiH , TFA, rt, 4 h		(79)	728
C_{22} 	Et_3SiH (3 eq), TFA, rt, 24 h		(55.5)	729

$\text{Ar} = 3,5\text{-(MeO)}_2\text{C}_6\text{H}_3$

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	Ph_3SiH (3 eq), TFA, rt, 48 h	 (87)	26
	Et_3SiH , TFA, CH_2Cl_2 , rt	(—)	730
	1. $t-Bu_2AlH$, hexanes, MeC_6H_5 , -78° 2. Et_3SiH (1.5 eq), $BF_3 \cdot OEt_2$ (1.1 eq), -20° , 24 h	 (65)	510
C_{23} 	Et_3SiH (4 eq), HOAc, reflux, 24 h	 (83)	29
C_{24} 	Et_3SiH , $BF_3 \cdot OEt_2$, CH_2Cl_2 , -78° to 0°	 (75)	181
	Et_3SiH , TFA, rt, 15 h	 I +  II 1 + II (45)	171

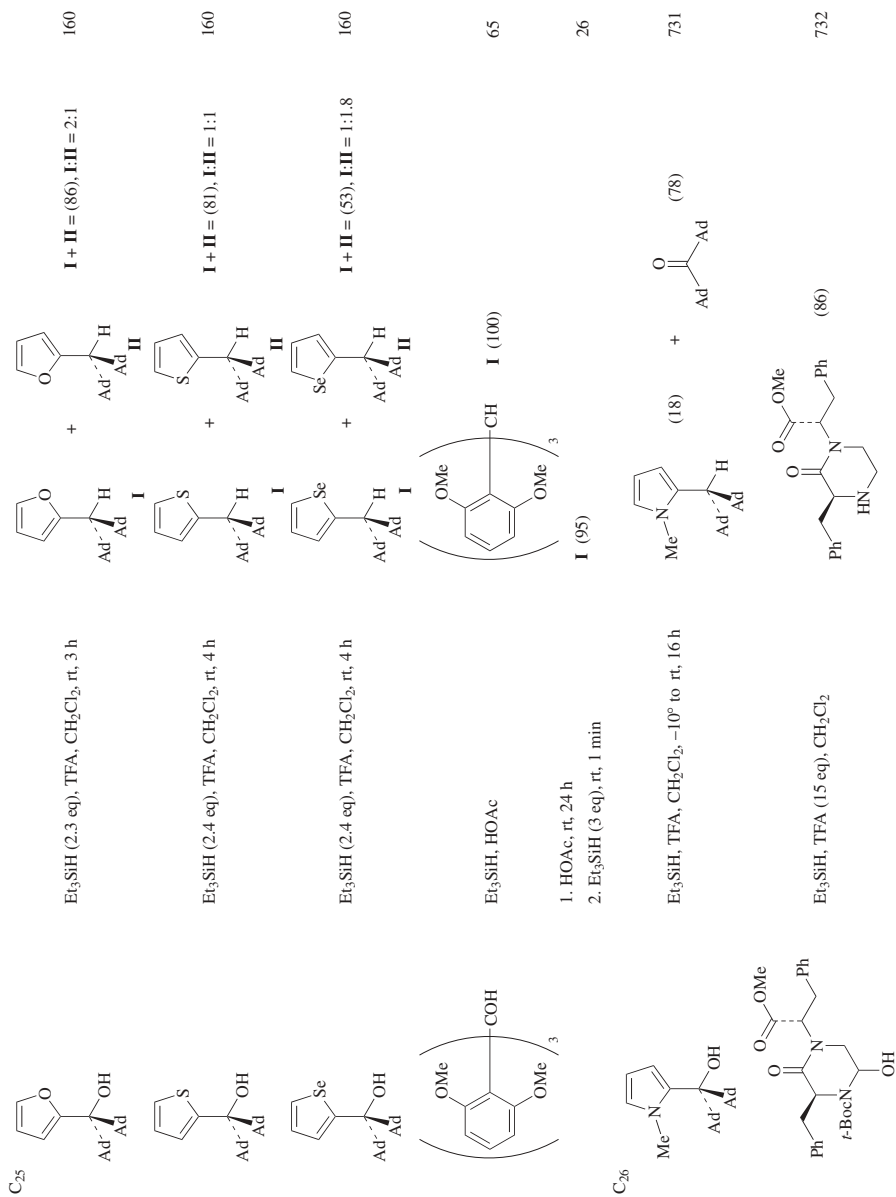
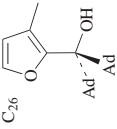
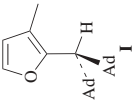
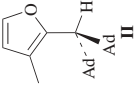
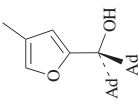
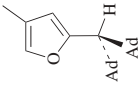
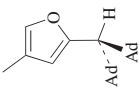
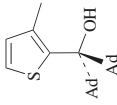
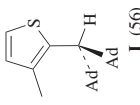
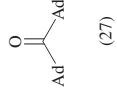
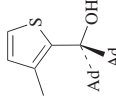
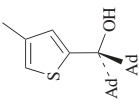
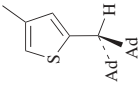
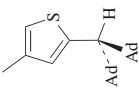
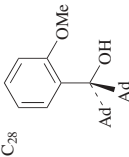
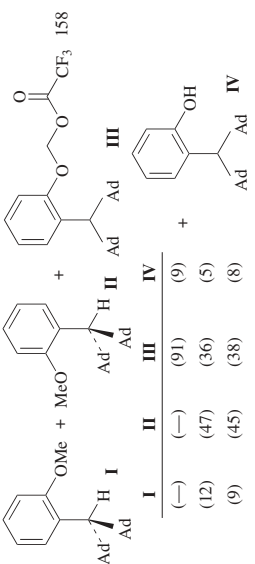
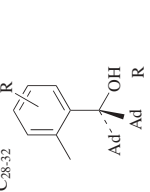
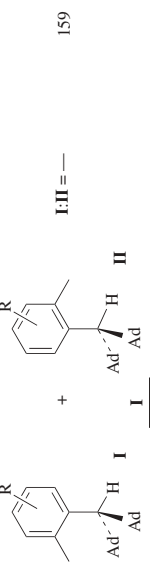


TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

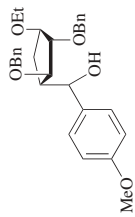
Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₆	Et ₃ SiH (3.0 eq), TFA, CH ₂ Cl ₂ , rt, 20 h	 I +  II I + II (30), I:II = 3 to 1:1	160
	Et ₃ SiH (2.4 eq), TFA, CH ₂ Cl ₂ , rt, 2 h	 I +  II I + II (58), I:II = 1:2	160
	Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 16 h	 I (56) +  (27)	160
	Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 2 h	I (93)	160
	Et ₃ SiH (2.4 eq), TFA, CH ₂ Cl ₂ , rt, 4 h	 I +  II I + II (82), I:II = 1:1	160

C_{27}		Et_3SiH or $PhMe_3SiH$, TFA, CH_2Cl_2		+		+		$(-)^b$ 161
C_{27-29}		Et_3SiH , TFA, rt		n = 11 (—) n = 13 (30)				733
C_{28}		Ph_2SiH_2 , TFA, CH_2Cl_2 , 3 h		+			$I + II$ (—), $I:II = 0.53$	159
							I	
							II	
							$I + II$ (—), $I:II = 0.32$	159
							$I + II$ (—), $I:II = 0.72$	159
							I (—) +	
							II (—)	159
							$I:II$	
		R_3Si					0.52	
		$n-C_6H_{13}H_2Si$					0.52	
		Ph_2HSi					0.49	
		Ph_3Si					0.60	
		$(i-Pr)_3Si$					0.41	
		Et_3Si					0.39	
		Me_2PhSi					5.4	
		$(TMS)_3Si$						

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

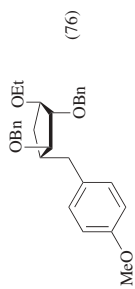
Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28} 	R_3SiH , TFA, CH_2Cl_2 , -10° to rt, 16 h		158
C_{28-32} 	Et_3SiH , TFA, CH_2Cl_2 , 3 h		159
	R_3Si	I (—) (12) (9) (0) (0) (8) (27) (21)	
	None	II (—) (47) (45) (37) (28) (41) (34) (9)	
	$n-C_6H_{13}H_2Si$	III (91) (36) (38) (49) (58) (40) (31) (54)	
	Ph_2HSi	IV (9) (5) (8) (15) (14) (11) (9) (17)	
	Ph_3Si		
	$(i-Pr)_3Si$		
	Et_3Si		
	Me_2PhSi		
	$(Me_3Si)_3Si$		
		I (—) (74) (79) (57) (94) (83) (66) (77) (71) (85)	
		II (—) (74) (79) (57) (94) (83) (66) (77) (71) (85)	
		III (—) (74) (79) (57) (94) (83) (66) (77) (71) (85)	
		IV (—) (74) (79) (57) (94) (83) (66) (77) (71) (85)	

C₂₉

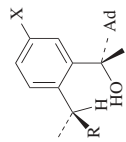


Et₃SiH, TFA, CH₂Cl₂, 0°, 2 h

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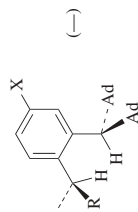


C₂₉₋₃₃



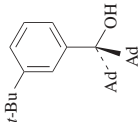
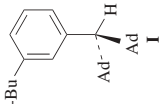
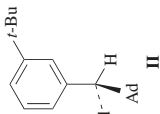
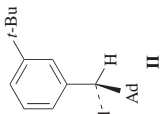
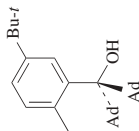
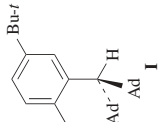
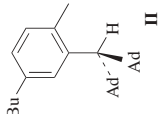
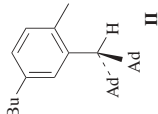
Et₃SiH (large xs), TFA

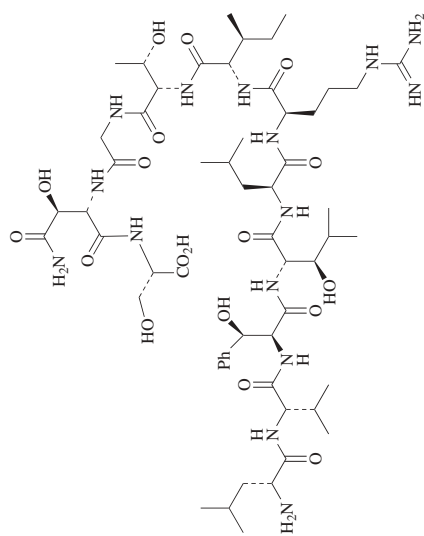
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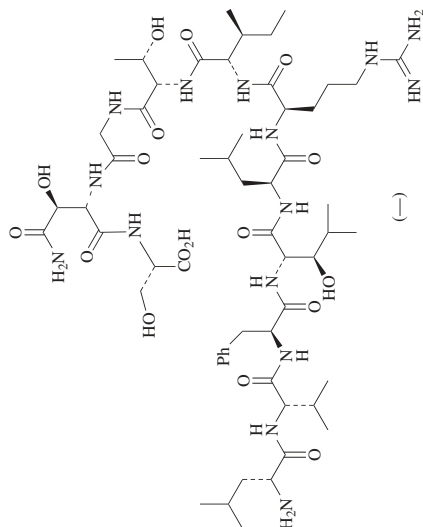
R, X = H, H; Me, *i*-Pr

TABLE 5. ORGANOSILANE REDUCTION OF ALCOHOLS (Continued)

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₁ 	R_3SiH , TFA, CH_2Cl_2 , 3 h	  +  (—) 159	159
	R_3Si $n-C_6H_{13}H_2Si$ Ph_3HSi Ph_3Si $(i-Pr)_3Si$ Et_3Si Me_2PhSi $(TMS)_3Si$	$I:II$ 0.74 1.3 2.5 21 3.4 4.1 23	
C ₃₂ 	R_3SiH , TFA, CH_2Cl_2 , 24 h	  +  (—) 159	159
	R_3Si $n-C_6H_{13}H_2Si$ Ph_3HSi Ph_3Si $(i-Pr)_3Si$ Et_3Si Me_2PhSi $(TMS)_3Si$	$I:II$ 2.9 5.8 1.6 NR 6.2 2.5 1.2	

C₅₇Et₃SiH, TFA





















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(—)

^a The yield was determined by gas chromatography.^b Various product ratios were observed for this reaction.

TABLE 6. ORGANOSILANE REDUCTION OF ETHERS

Ether	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅ 	Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 (97)	144, 145
C ₆ 	Et ₃ SiH (1.1 eq), (C ₆ F ₅) ₃ B (10 mol%), CH ₂ Cl ₂ , rt, 20 h	 OH (88)	144, 145
	Et ₃ SiH (1.1 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 -OSiEt ₃ (>95) + C ₃ H ₈	144, 145
	Et ₃ SiH (2 eq), TFA (10 eq), reflux, 24 h	 OH (60)	271
C ₇ 	Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (10 mol%), CH ₂ Cl ₂ , rt, 20 h; then TBAF	 OH (91)	144
	Et ₃ SiH (1.1 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 OSiEt ₃ (>99) + CH ₄	145
	Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h; then TBAF	 OH (79)	145
C ₈ 	Et ₃ SiD (1.5 eq), (C ₆ F ₅) ₃ B (5 mol%), C ₆ H ₁₄ , rt, 20 h	 D (—) 41% ee	145
	Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 (78)	145
	Et ₃ SiH (1.1 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 OSiEt ₃ (>99)	145

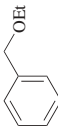
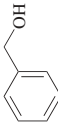
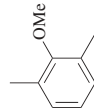



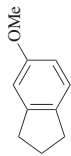
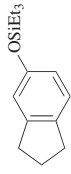


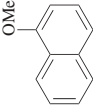

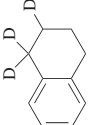
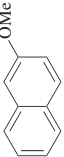

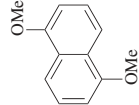

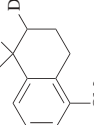
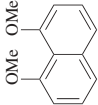
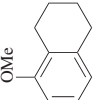
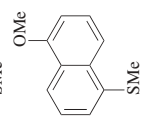
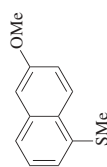
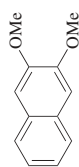
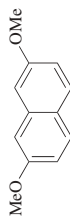
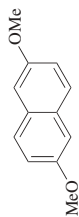
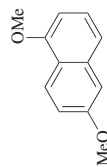
C ₉		Et ₃ SiH (2 eq), TFA (10 eq), reflux, 24 h	 (7)	271
C ₉₋₁₆		Et ₃ SiH (1.1 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 (>99) + CH ₄	145
		PMHS (2 eq), (Ph ₃ P) ₄ Pd (0.01 eq), THF, rt, 3-5 h	ROH + 	270
			R	
			Ph(CH ₂) ₃	(94)
			PhMeCH	(87)
			Ph ₂ CH	(85)
			2- <i>i</i> -Pr-4-Me- <i>c</i> -C ₆ H ₉	(89)
			2-C ₁₀ H ₇	(90)
			4-FC ₆ H ₄	(92)
			4-MeOC ₆ H ₄	(90)
			4-NO ₂ -C ₆ H ₄	(88)
			Prenylo(CH ₂) ₄	(92)
			BnO(CH ₂) ₄	(90)
			PMBO(CH ₂) ₄	(87)
			TsO(CH ₂) ₄	(92)
			THPO(CH ₂) ₄	(85)
			AcO(CH ₂) ₄	(89)
			MOMO(CH ₂) ₄	(85)
			TBSO(CH ₂) ₄	(90)
C ₁₀		Et ₃ SiH (1.1 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 OSiEt ₃	145
C ₁₁		PMHS (2 eq), (Ph ₃ P) ₄ Pd (0.01 eq), THF, rt, 3-5 h	EtO ₂ C-  -OH (86)	270

TABLE 6. ORGANOSILANE REDUCTION OF ETHERS (Continued)

Ether	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 	Et ₃ SiH (1.3 eq), BF ₃ •OH ₂ (4-6 eq), CH ₂ Cl ₂ , rt, 10 h	 1 (37)	217
	Et ₃ SiD (6.4 eq), BF ₃ •OH ₂ (12.8 eq), CH ₂ Cl ₂ , rt, 24 h	 (100)	262
	Et ₃ SiH (1.3 eq), BF ₃ •OH ₂ (4-6 eq), CH ₂ Cl ₂ , rt, 10 h	1 (26)	217
	Et ₃ SiD (6.4 eq), BF ₃ •OH ₂ (12.8 eq), CH ₂ Cl ₂ , rt, 24 h	 (100)	262
C ₁₂ 	Et ₃ SiH (6.4 eq), BF ₃ •OH ₂ (12.8 eq), CH ₂ Cl ₂ , rt, 6 h	 (100)	262
	Et ₃ SiD (6.4 eq), BF ₃ •OH ₂ (12.8 eq), CH ₂ Cl ₂ , rt, 24 h	 (100)	262
	Et ₃ SiH (6.4 eq), BF ₃ •OH ₂ (12.8 eq), CH ₂ Cl ₂ , rt, 6 h	 (100)	262



Et₃SiH (6.4 eq), BF₃•OH₂ (12.8 eq),
CH₂Cl₂, rt, 24 h

Et₃SiH (6.4 eq), BF₃•OH₂ (12.8 eq),
CH₂Cl₂, rt, 24 h

Et₃SiD (6.4 eq), BF₃•OH₂ (12.8 eq),
CH₂Cl₂, rt, 37 h

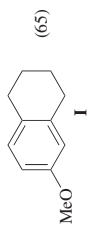
Et₃SiH (6.4 eq), BF₃•OH₂ (12.8 eq),
CH₂Cl₂, rt, 6 h

Et₃SiH (6.4 eq), BF₃•OH₂ (12.8 eq),
CH₂Cl₂, rt, 48 h

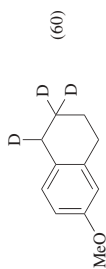
Et₃SiD (6.4 eq), BF₃•OH₂ (12.8 eq),
CH₂Cl₂, rt, 144 h

Et₃SiH (6.4 eq), BF₃•OH₂ (12.8 eq),
CH₂Cl₂, rt, 24 h

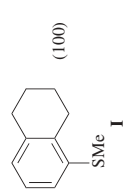
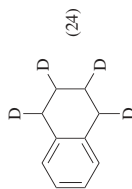
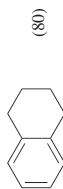
Et₃SiH (3-5 eq), BF₃•OH₂ (12.8 eq),
CH₂Cl₂, 0°, 24 h



I (95)



I (50)



I (100)

262

262

262

262

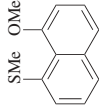
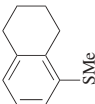


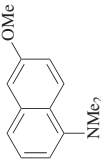
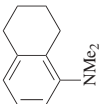
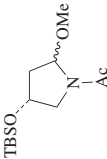
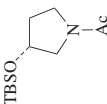


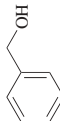
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262

262

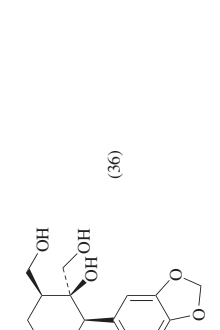
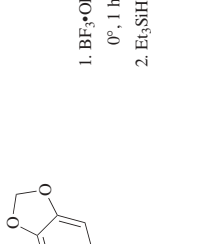
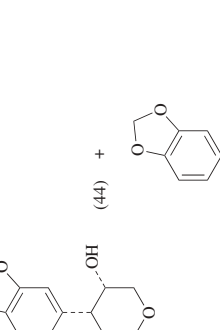
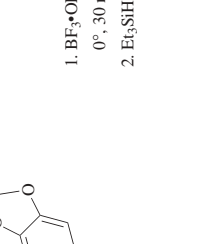


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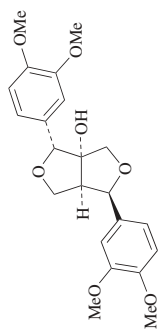
TABLE 6. ORGANOISILANE REDUCTION OF ETHERS (Continued)

	Ether	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂		Et ₃ SiH (3-5 eq), BF ₃ •OEt ₂ , CH ₂ Cl ₂ , 0°, 24 h	 (70)	263
		Et ₃ SiH (2 eq), TFA, rt, 20 min	 (88)	179
C ₁₃		Et ₃ SiH (6.4 eq), BF ₃ •OEt ₂ , CH ₂ Cl ₂ , rt, 24 h	 (100)	262
		Et ₃ SiH (2 eq), BF ₃ •OEt ₂ (2 eq), CH ₂ Cl ₂ , -40°, 1-2 h	 (97)	521
C ₁₄		Et ₃ SiH (1.1 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 (77) + I (86)	145
		Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	I (86)	145
		Et ₃ SiH (2 eq), TFA (10 eq), reflux, 24 h	 (3)	271

C ₁₅		Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 45 min	(96) + Me ₃ CH	307
C ₁₆		PMHS (2 eq), (Ph ₃ P) ₄ Pd (0.01 eq), THF, rt, 3-5 h	(85)	270
		Et ₃ SiH (2 eq), TFA (10 eq), reflux, 24 h	(60)	271
C ₂₀		Et ₃ SiH (1.1 eq), (C ₆ F ₅) ₃ B (10 mol%), CH ₂ Cl ₂ , rt, 20 h	I <i>n</i> -C ₁₀ H ₂₂ (93) + <i>n</i> -C ₁₀ H ₂₁ OSiEt ₃ (95)	144
		Et ₃ SiH (3.0 eq), (C ₆ F ₅) ₃ B (10 mol%), CH ₂ Cl ₂ , rt, 20 h	I (>99)	144
		Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 35 min	(100) + Me ₃ CH	307

TABLE 6. ORGANOSILANE REDUCTION OF ETHERS (Continued)

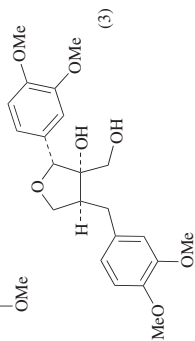
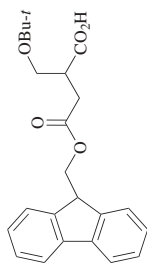
C ₂₀	Ether	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. BF ₃ •OEt ₂ (2.25 eq), CH ₂ Cl ₂ , 0°, 1 h 2. Et ₃ SiH (13.9 eq), rt, 16 h	 (36)	735
		1. BF ₃ •OEt ₂ (2.25 eq), CH ₂ Cl ₂ , 0°, 30 min 2. Et ₃ SiH (23 eq), rt, 16 h	 (44)	735
C ₂₁		Et ₃ SiH (4 eq), TFA, rt, 3 h	 (80)	179

C₂₂

Et₃SiH (4.5 eq),
BF₃•OEt₂ (1.5 eq), CH₂Cl₂,
0°, 1 h; rt, 16 h

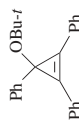
484, 736

(66) +

C₂₃

Et₃SiH (2.5 eq), TFA,
CH₂Cl₂, rt, 15 min

307

(99) + Me₃CHC₂₅

Et₃SiH (3 eq), HOAc, rt, 48 h

26

(80)


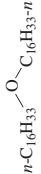
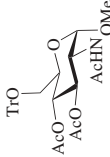
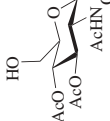
Et₃SiH, TFA

272

I (45)

I

TABLE 6. ORGANO-SILANE REDUCTION OF ETHERS (Continued)

Ether	Conditions	Product(s) and Yield(s) (%)	Refs.
C₃₀₋₄₄			
	Et_3SiH (1.2 eq), Et_3SiOTf (x eq), CH_2Cl_2 , rt	$\text{RO}-\text{CH}_2-\text{CH}_2-\text{OH}$ + Ph_3CH	269
R	x		
Ac	0.005 4 min, 30 sec	(96)	
Piv	0.02 2 min	(99)	
Bz	0.01 3 min, 30 sec	(95)	
Bn	0.01 1 min, 20 sec	(93)	
MPM	0.01 1 min, 16 sec	(93)	
TBDPS	0.01 4 min	(89)	
MOM	0.01 24 min	(93)	
C₃₂			
	Et_3SiH (1.1 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 20 h	$n\text{-C}_{16}\text{H}_{34}$ (98) + $n\text{-C}_{16}\text{H}_{33}\text{OSiEt}_3$ (98)	145
		I	
	Et_3SiH (3.0 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 20 h	I (95)	145
	Et_3SiH (3.6 eq), TMSOTf (0.01 eq), CH_2Cl_2 , rt, 32 min	 (86) + Ph_3CH	269

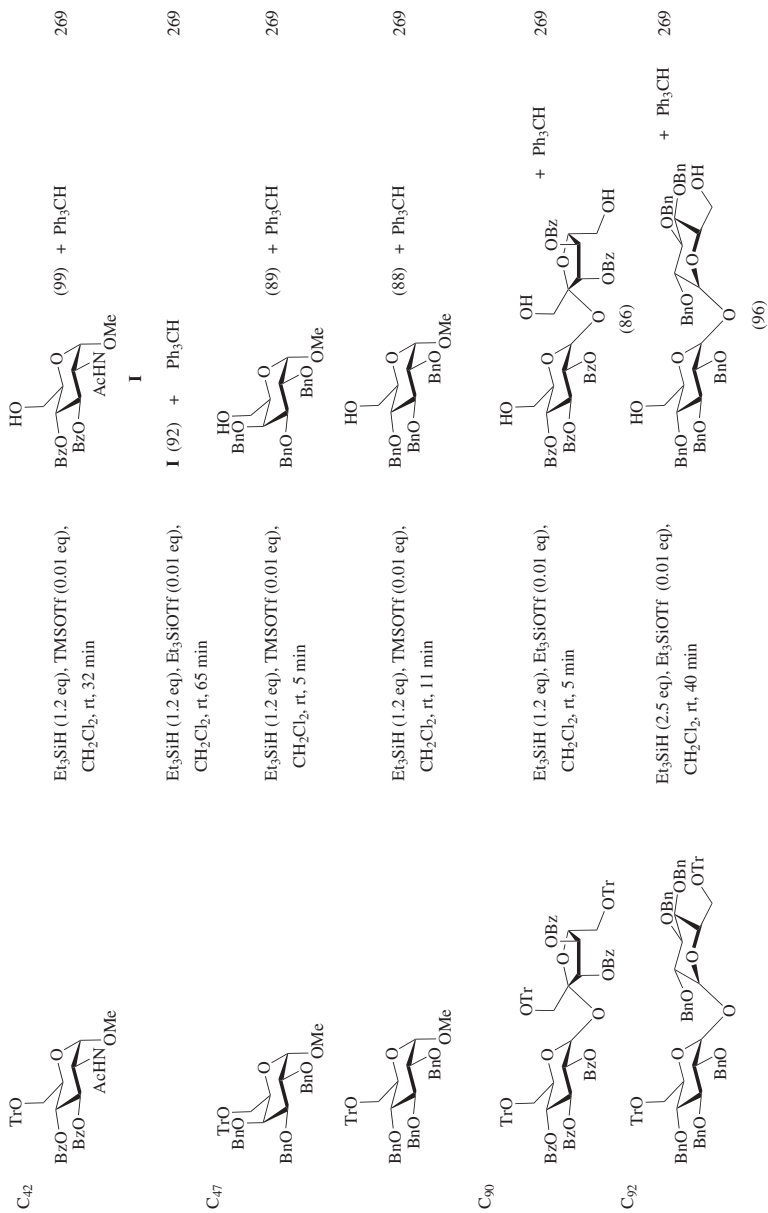


TABLE 7. ORGANOSILANE REDUCTION OF ALLYL ESTERS

Allyl Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	PMHS (2 eq), (Ph ₃ P) ₄ Pd (0.01 eq), THF, rt, 3-5 h	(87) + (—)	270
	Et ₃ SiH, TFA, CH ₂ Cl ₂ , BF ₃ •OEt ₂	(—)	275
C ₁₁ 	PMHS (2.0 eq), (Ph ₃ P) ₄ Pd (4.0 mol%), THF, rt, 4 d	I + II (98), I:II = 1:1 II	196, 273
	Ph ₂ SiH ₂ (2.5 eq), ZnCl ₂ (2.1 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 2 h	I + II (75), I:II = 33:67	273
	Ph ₂ SiH ₂ (2.1 eq), ZnCl ₂ (1.8 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 3 h	I + II (92), I:II = 44:56	273
	Ph ₂ SiH ₂ (2 eq), ZnCl ₂ (2.4 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 4 h	I + II (68), I:II = 50:50	273
	Ph ₂ SiH ₂ (2 eq), ZnCl ₂ (1.9 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 5 h	I + II (63), I:II = 75:25	273

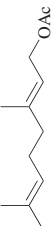


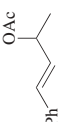
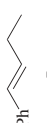

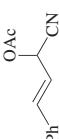

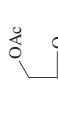


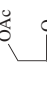
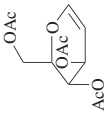
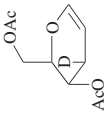
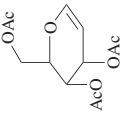
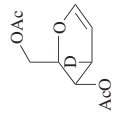
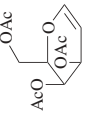
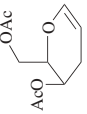

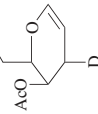
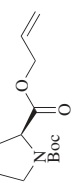
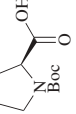

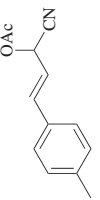
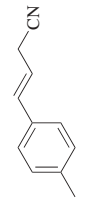
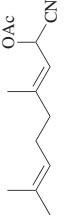
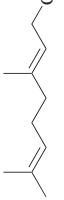

	PMHS (1.75 eq), (Ph ₃ P) ₄ Pd (6 mol%), PPh ₃ (20 mol%), THF, 5 d		(52) + 	273
	PMHS (1.7 eq), (Ph ₃ P) ₄ Pd (5.0 mol%), THF, rt, 5 d	I + II (99), I:II = 1:1		196
	Ph ₂ SiH ₂ (2.0 eq), ZnCl ₂ (3–4 eq), (Ph ₃ P) ₄ Pd (7.2 mol%), THF, rt, 30 h	I + II (99), I:II = 1:1		196
	PMHS (2.1 eq), (Ph ₃ P) ₄ Pd (4.0 mol%), THF, rt, 24 h		+ 	196
	Ph ₂ SiH ₂ (2.0 eq), (Ph ₃ P) ₄ Pd (10 mol%), THF, 0°, 24 h	I + II (100), I:II = 6:4		196
	PMHS (2.2 eq), (Ph ₃ P) ₄ Pd (4.6 mol%), THF, 20 min		(93)	273
	Ph ₂ SiH ₂ (1.7 eq), ZnCl ₂ (2 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 3 h		+ 	273
	Ph ₂ SiH ₂ (4 eq), ZnCl ₂ (2.2 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 24 h		(58)	273
	Ph ₂ SiH ₂ (3.5 eq), ZnCl ₂ (3–4 eq), (Ph ₃ P) ₄ Pd (12.0 mol%), THF, rt, 13 h; 50°, 2 h	I (90)		196

TABLE 7. ORGANOSILANE REDUCTION OF ALLYL ESTERS (Continued)

Allyl Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₂	Ph ₂ SiD ₂ (2.6 eq), ZnCl ₂ (5.4 eq), [(p-tol) ₃ P]Pd, 24 h	 (59)	273
 C ₁₃	Ph ₂ SiD ₂ (4 eq), ZnCl ₂ (8 eq), [(p-tol) ₃ P]Pd, 24 h	 (42)	273
 C ₁₃	Ph ₂ SiH ₂ (2 eq), ZnCl ₂ (4 eq), [(p-tol) ₃ P]Pd, 120 h	 (26)	273
 C ₁₃	Ph ₂ SiD ₂ (2.7 eq), ZnCl ₂ (8.4 eq), [(p-tol) ₃ P]Pd, 80 h	 (10)	273
 C ₁₃	PMHS (2 eq), (Ph ₃ P) ₄ Pd (0.01 eq), THF, rt, 3-5 h	 (85) +  (—)	270
 C ₁₃	PMHS (1.8 eq), (Ph ₃ P) ₄ Pd (3 mol%), THF, 1.5 h	 (100)	273
 C ₁₃	PMHS (2.5 eq), (Ph ₃ P) ₄ Pd (3.5 mol%), THF, 48 h	 I +  II	273

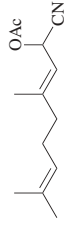
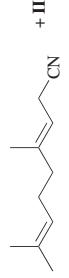
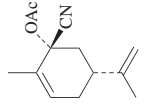
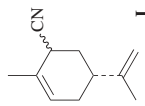
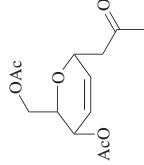
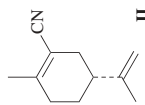
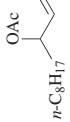
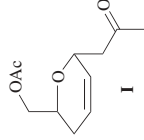
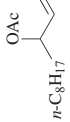

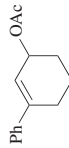

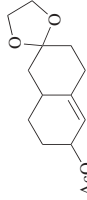
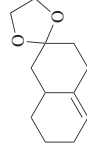
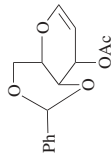
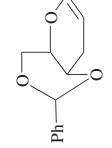
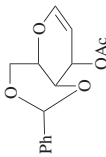
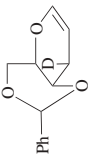
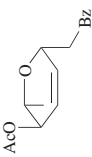
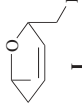
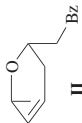
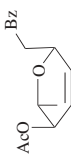
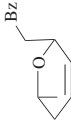
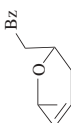
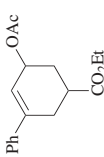
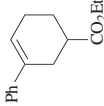
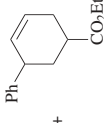
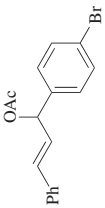
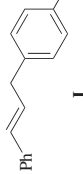
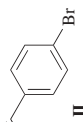
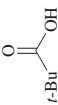
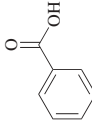
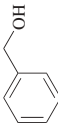
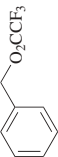
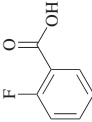
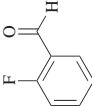


	PMHS (2.5 eq), (Ph ₃ P) ₄ Pd (3.5 mol%), THF, rt, 48 h		I + II (75), I:II = 10:1	196
	Ph ₂ SiH ₂ (2.2 eq), (Ph ₃ P) ₄ Pd (7.2 mol%), THF, rt, 30 h		I (90) + II (10%)	196
	Ph ₂ SiH ₂ (3.5 eq), ZnCl ₂ (3–4 eq), (Ph ₃ P) ₄ Pd (12.0 mol%), THF, rt, 4 h		I + II (73), I:II = 1:1	196
	Ph ₂ SiH ₂ (2 eq), ZnCl ₂ (1.9 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 4 h		I + II (65), I:II = 50:50	273
	PMHS (3.7 eq), (Ph ₃ P) ₄ Pd (8.0 mol%), THF, rt, 1.5 h		(74)	196, 273
	Et ₃ SiH (3 eq), LiClO ₄ , Et ₂ O, rt, 16 h		(92)	173
	Et ₃ SiH (3 eq), LiClO ₄ , Et ₂ O, rt, 16 h		(48) + (12)	173
	Ph ₂ SiH ₂ (3.3 eq), ZnCl ₂ (5 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 10 h		(63)	273

TABLE 7. ORGANOSILANE REDUCTION OF ALLYL ESTERS (Continued)

Allyl Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 	Ph ₂ SiD ₂ (3.7 eq), ZnCl ₂ (16.9 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 10 h	 (55)	273
C ₁₆ 	Ph ₂ SiH ₂ (2.9 eq), ZnCl ₂ (2.4 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 4 h	 I +  II I + II (79), I:II = 50:50	273
	Ph ₂ SiH ₂ (2.9 eq), ZnCl ₂ (2.4 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 4 h	 I +  II I + II (79), I:II = 50:50	273
C ₁₇ 	Et ₃ SiH (3 eq), LiClO ₄ , Et ₂ O, rt, 16 h	 (89) +  (5)	173
	PMHS (1.8 eq), (Ph ₃ P) ₄ Pd (3 mol%), THF, 1.5 h	 I +  II I + II (89), I:II = 1:1	196, 273
	Ph ₂ SiH ₂ (1.9 eq), (Ph ₃ P) ₄ Pd (5.7 mol%), THF, rt, 1 h	I + II (90), I:II = 1:1	196





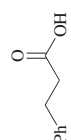

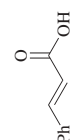

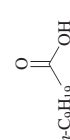

C ₁₈		Ph ₂ SiH ₂ (1.4 eq), ZnCl ₂ (2.4 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 4 h		I + II (94), I:II = 50:50	273
C ₂₀		Ph ₂ SiH ₂ (1.6 eq), ZnCl ₂ (2.4 eq), [(<i>p</i> -tol) ₃ P] ₄ Pd, 6 h		I + II (91), I:II = 50:50	273
C ₂₆		PMHS (2 eq), (Ph ₃ P) ₄ Pd (0.01 eq), THF, rt, 3-5 h		(85) +	270
C ₂₆		PMHS (2 eq), (Ph ₃ P) ₄ Pd (0.01 eq), THF, rt, 3-5 h		(87) +	270
C ₄₀		Et ₃ SiH, TMSOTf, CH ₂ Cl ₂ , 0-20°, 23 h		(16)	737

TABLE 8. ORGANOSILANE REDUCTION OF ACIDS

Carboxylic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	Et_3SiH (2 eq), TFA (10 eq), TFAA 60° , 5 h	$t\text{-Bu}-CH_2-O_2CCF_3$ I (70)	277
C_7 	Ph_2SiH_2 (2 eq), TFA (10 eq), TFAA, 60° , 5 h 1. $EtMe_2SiH$ (4 eq), 201 (1 mol%), 1,4-dioxane, 20° , 0.5 h 2. Add acid, 18 h	I (80)  (46)	277
	Et_3SiH (xs), TFA, TFAA, 60° , 5 h	 (30)	277
	B , $>180^\circ$	 I (72)	284
C_{7-10} 	A , $150\text{--}170^\circ$ PMHS (3 eq), TBAF (2 mol%), THF, τ	I (60) 	284
		Ar Ph (82) 4- BrC_6H_4 (74) 4- ClC_6H_4 (67) 2,4- $Cl_2C_6H_3$ (69) 3,5- $Cl_2C_6H_3$ (75) 3- MeC_6H_4 (78) 4- MeC_6H_4 (70) 2,4- $Me_2C_6H_3$ (72) 3,4,5-(MeO) $_3C_6H_2$ (79)	278









C _{7:11}	<div><div><div>O</div><div> </div><div>Ar-C(=O)OH</div></div></div>	Et ₃ SiH (3.3 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	Ar-CH ₂ -OSiEt ₃	<table><tr><th>Ar</th><th></th></tr><tr><td>Ph</td><td>(95)</td></tr><tr><td>4-FC₆H₄</td><td>(93)</td></tr><tr><td>4-BrC₆H₄</td><td>(93)</td></tr><tr><td>4-IC₆H₄</td><td>(94)</td></tr><tr><td>4-MeC₆H₄</td><td>(91)</td></tr><tr><td>2-C₁₀H₇</td><td>(96)</td></tr></table>	Ar		Ph	(95)	4-FC ₆ H ₄	(93)	4-BrC ₆ H ₄	(93)	4-IC ₆ H ₄	(94)	4-MeC ₆ H ₄	(91)	2-C ₁₀ H ₇	(96)	281, 282		
Ar																					
Ph	(95)																				
4-FC ₆ H ₄	(93)																				
4-BrC ₆ H ₄	(93)																				
4-IC ₆ H ₄	(94)																				
4-MeC ₆ H ₄	(91)																				
2-C ₁₀ H ₇	(96)																				
C _{7:18}	<div><div><div>O</div><div> </div><div>R-C(=O)OH</div></div></div>	Et ₃ SiH (6 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	RMe	<table><tr><th>R</th><th></th></tr><tr><td>Ph</td><td>(85)</td></tr><tr><td>BnCH₂</td><td>(91)</td></tr><tr><td>Bn(CH₂)₂</td><td>(37)</td></tr><tr><td>Bn(CH₂)₃</td><td>(86)</td></tr><tr><td>Bn(CH₂)₄</td><td>(88)</td></tr><tr><td><i>n</i>-C₁₁H₂₃</td><td>(94)</td></tr><tr><td><i>n</i>-C₁₇H₃₅</td><td>(91)</td></tr></table>	R		Ph	(85)	BnCH ₂	(91)	Bn(CH ₂) ₂	(37)	Bn(CH ₂) ₃	(86)	Bn(CH ₂) ₄	(88)	<i>n</i> -C ₁₁ H ₂₃	(94)	<i>n</i> -C ₁₇ H ₃₅	(91)	281
R																					
Ph	(85)																				
BnCH ₂	(91)																				
Bn(CH ₂) ₂	(37)																				
Bn(CH ₂) ₃	(86)																				
Bn(CH ₂) ₄	(88)																				
<i>n</i> -C ₁₁ H ₂₃	(94)																				
<i>n</i> -C ₁₇ H ₃₅	(91)																				
	<div><div><div>O</div><div> </div><div>R-C(=O)OH</div></div></div>	PMHS (10 eq), Ti(OEt) ₄ (100 mol%), THF, 16 h	R-CH ₂ -OH	<table><tr><th>R</th><th></th></tr><tr><td>Ph</td><td>(92)</td></tr><tr><td>4-O₂NC₆H₄</td><td>(78)</td></tr><tr><td>4-HOC₆H₄</td><td>(81)</td></tr><tr><td>Bn</td><td>(81)</td></tr><tr><td><i>n</i>-C₁₇H₃₅</td><td>(86)</td></tr></table>	R		Ph	(92)	4-O ₂ NC ₆ H ₄	(78)	4-HOC ₆ H ₄	(81)	Bn	(81)	<i>n</i> -C ₁₇ H ₃₅	(86)	279				
R																					
Ph	(92)																				
4-O ₂ NC ₆ H ₄	(78)																				
4-HOC ₆ H ₄	(81)																				
Bn	(81)																				
<i>n</i> -C ₁₇ H ₃₅	(86)																				

TABLE 8. ORGANOSILANE REDUCTION OF ACIDS (Continued)

Carboxylic Acid	Conditions	R	Product(s) and Yield(s) (%)		Refs.
			R	Time	
$C_{7,18}$ 	PMHS (10 eq), Ti(OPr- <i>i</i>) ₄ (14 mol%), THF		Ph	16 h (63)	279
			4-O ₂ NC ₆ H ₄	16 h (86)	
			4-MeC ₆ H ₄	30 h (69)	
			4-MeOC ₆ H ₄	48 h (76)	
C_8 	Et ₃ SiH (xs), TFA, TFAA, 60°, 5 h		Ar		283
			4-MeOC ₆ H ₄ (97)		
			4-MeC ₆ H ₄ (45)		
C_9 	Et ₃ SiH (6.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h		(94)		282
	1. EtMe ₂ SiH (4 eq), 223 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add acid, 0.5 h B , >180°		(72)		280
			(50)		
			I (65)		
C_{10} 	A, 150-170° 1. EtMe ₂ SiH (4 eq), 223 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add acid, 6 h		(80)		280

C ₁₁		Et ₃ SiH (6.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 + 	I + II (—), II = 37:63	282
C ₁₁		Et ₃ SiH (6.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h			282
C ₁₂		Et ₃ SiH (6.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	<i>n</i> -C ₁₁ H ₂₄ (91)		282
C ₁₂		Et ₃ SiH (6.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h			282
C ₁₇		Et ₃ SiH (6.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	<i>n</i> -C ₁₇ H ₃₆ (94)		282

TABLE 9. ORGANOSILANE REDUCTION OF ACYL HALIDES

Acyl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₋₁₂ 	C, rt	 R Me (—) <i>i</i> -Bu (—) Ph (90) BnCH ₂ (87) PhCH=CH (86) 4-O ₂ NC ₆ H ₄ (90) 4-MeOC ₆ H ₄ (91) 2-C ₄ H ₃ O (87) 2-C ₄ H ₃ S (86) Br(CH ₂) ₃ (90) Cl(CH ₂) ₃ (82) EtO ₂ C(CH ₂) ₈ (80) (>95) ^d	109
C ₃ 	A, rt		109
C ₇ 	Bn ₃ SiH, Et ₂ O, reflux	 I (—)	286
	Et ₃ SiH, AlCl ₃ , Et ₂ O, reflux	I (—)	286
	Et ₃ SiH (6 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	PhMe (84)	281
	Cl ₃ SiH (3 eq), (<i>n</i> -Pr) ₃ N (1 eq), MeCN, rt, 1 h; 85°, 0.5 h	 (91)	711
	Bn ₃ SiH, Et ₂ O, reflux	I (—)	286
	Et ₃ SiH, Et ₂ O, reflux	I (—)	286
	A, rt	I (45) ^d	109

C ₇		Et ₃ SiH, AlCl ₃ , Et ₂ O, reflux		(—)	286
C ₈		C, rt		(89)	109
		C, rt		(15) ^a	109
		A, rt		I (89)	109
		C, rt		(85)	109
		C, rt		(>95) ^a	109
C ₉		Br ₃ SiH, Et ₂ O, reflux		(—)	286
		X = Cl, Br			

TABLE 9. ORGANOSILANE REDUCTION OF ACYL HALIDES (Continued)

Acyl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	C, rt	 (85)	109
C ₁₁ 	Et ₃ SiH (2.2 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	 (95)	281, 282
C ₁₄ 	Et ₃ SiH (4.0 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	<i>n</i> -C ₁₄ H ₃₀ (97)	282
C ₁₆ 	Et ₃ SiH (4 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	<i>n</i> -C ₁₆ H ₃₄ (95)	281
C ₂₂ 	Et ₃ SiH, TFA, CCl ₄ , 15 min	 (—)	285

^a The yield was determined by NMR analysis.

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES



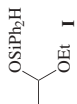
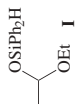
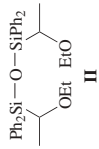

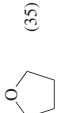

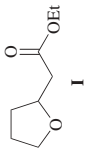
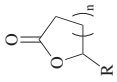
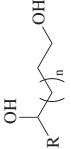

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₄	Ph ₂ MeSiH (1.2 eq), Mn(CO) ₅ Ac (3.0 mol%), C ₆ D ₆ , rt, 1.75 h	 (84)	295
	PhSiH ₃ (1.2 eq), Mn(CO) ₄ PPh ₃ Ac (1.5-3.0 mol%), C ₆ D ₆ , rt, 15 min	Et ₂ O (85) + PhSiH(OEt) ₂ (—)	295
	PhSiH ₃ (1.2 eq), Mn(CO) ₅ Ac (1.5-3.0 mol%), C ₆ D ₆ , rt, 1.5 h	Et ₂ O (100)	295
	PhSiH ₃ (1.2 eq), Mn(CO) ₅ Br (1.5-3.0 mol%), C ₆ D ₆ , rt, 4 h	Et ₂ O (55)	295
	Ph ₂ SiH ₂ (1.2 eq), Mn(CO) ₄ PPh ₃ Ac (1.5-3.0 mol%), C ₆ D ₆ , rt, 4 h	 (95) + Ph ₂ SiH(OEt) (5)	295
	Ph ₂ SiH ₂ (1.2 eq), Mn(CO) ₅ Ac (1.5-3.0 mol%), C ₆ D ₆ , rt, 4 h	 I +  II I + II (—), I:II = 2:1	295
	Ph ₂ SiH ₂ (1.2 eq), Mn(CO) ₅ SiMe ₂ Ph (3.0 mol%), C ₆ D ₆ , hv, 20°, 35 min	Et ₂ O (100)	295
	Et ₃ SiH (2.2 eq), 201 (0.2 mol%), rt, 26 h	EtOSiEt ₃ (94) + EtOEt (<1)	377
	PhSiH ₃ (1.2 eq), Mn(CO) ₅ Br (1.5-3.0 mol%), C ₆ D ₆ , rt, 25 min	 (35)	295

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.																												
C ₄ 	OTBS $\text{CH}_2=\text{C}(\text{OTBS})\text{CO}_2\text{Et}$ 1. $\text{OEt}, \text{SbCl}_5, \text{TMSCl}, \text{SnI}_2, \text{CH}_2\text{Cl}_2, -78^\circ, 30 \text{ min}$ 2. $\text{Et}_3\text{SiH} (1.5 \text{ eq}), -23^\circ, 2.5 \text{ h}$	 I (75)	306																												
C _{4,5} $\text{R}^1-\text{C}(=\text{O})\text{OR}^2$	OTBS $\text{CH}_2=\text{C}(\text{OTBS})\text{CO}_2\text{Et}$ 1. $\text{OEt}, \text{TrSbCl}_6 (5\text{--}30 \text{ mol}\%), \text{CH}_2\text{Cl}_2, -78^\circ, 30 \text{ min}$ 2. $\text{Et}_3\text{SiH} (1.5 \text{ eq}), -23^\circ, 2.5 \text{ h}$	I (72)	306																												
C _{4,6} 	$\text{Cl}_3\text{SiH}, \gamma\text{-irradiation}$	<table border="1"> <thead> <tr> <th>R¹</th><th>R²</th><th>n</th><th>R</th></tr> </thead> <tbody> <tr> <td>H</td><td><i>n</i>-Pr</td><td>0</td><td>Me</td></tr> <tr> <td>Me</td><td>Et</td><td>1</td><td>Me</td></tr> <tr> <td>Me</td><td><i>n</i>-Pr</td><td>2</td><td>H</td></tr> <tr> <td>Et</td><td>Me</td><td>3</td><td>H</td></tr> <tr> <td>Et</td><td>Et</td><td></td><td></td></tr> <tr> <td>Et</td><td><i>n</i>-Pr</td><td></td><td></td></tr> </tbody> </table>	R ¹	R ²	n	R	H	<i>n</i> -Pr	0	Me	Me	Et	1	Me	Me	<i>n</i> -Pr	2	H	Et	Me	3	H	Et	Et			Et	<i>n</i> -Pr			296
R ¹	R ²	n	R																												
H	<i>n</i> -Pr	0	Me																												
Me	Et	1	Me																												
Me	<i>n</i> -Pr	2	H																												
Et	Me	3	H																												
Et	Et																														
Et	<i>n</i> -Pr																														
C _{4,9} $\text{R}^1-\text{C}(=\text{O})\text{OR}^2$	$(\text{MeO})_3\text{SiH} (3.0 \text{ eq}), \text{LiOMe} (8 \text{ mol}\%), \text{THF}, \text{rt}, 0.5 \text{ h}$ $\text{Et}_3\text{SiH} (1.5 \text{ eq}), \text{Ru catalyst} (1 \text{ mol}\%), \text{MeC}_6\text{H}_5, 100^\circ, 16 \text{ h}$	 	294																												
C _{4,9} $\text{R}^1-\text{C}(=\text{O})\text{OR}^2$			299																												

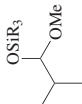
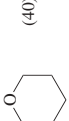

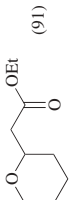


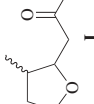
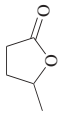
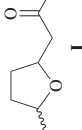

R ¹	R ²	Catalyst			
Et	Me	Ru ₃ (CO) ₁₂	(57)		
Et	Me	[RuCl ₂ (CO) ₃] ₂ , EtI, Et ₂ NH (5 eq)	(57)		
Me	<i>i</i> -Pr	Ru ₃ (CO) ₁₂	(74)		
Me	<i>i</i> -Pr	[RuCl ₂ (CO) ₃] ₂ , EtI, Et ₂ NH (5 eq)	(91)		
Me	<i>n</i> -Bu	Ru ₃ (CO) ₁₂	(45)		
<i>n</i> -Bu	Me	[RuCl ₂ (CO) ₃] ₂ , EtI, Et ₂ NH (5 eq)	(66)		
<i>c</i> -C ₆ H ₁₁	Me	Ru ₃ (CO) ₁₂	(61)		
<i>c</i> -C ₆ H ₁₁	Me	[RuCl ₂ (CO) ₃] ₂ , EtI, Et ₂ NH (5 eq)	(97)		
Me	Ph	Ru ₃ (CO) ₁₂	(94)		
Me	Ph	[RuCl ₂ (CO) ₃] ₂ , EtI, Et ₂ NH (5 eq)	(98)		
Ph	Me	Ru ₃ (CO) ₁₂	(57) ^a		
Ph	Me	[RuCl ₂ (CO) ₃] ₂ , EtI, Et ₂ NH (5 eq)	(63) ^a		
Bn	Me	Ru ₃ (CO) ₁₂	(84)		
Bn	Me	[RuCl ₂ (CO) ₃] ₂ , EtI, Et ₂ NH (5 eq)	(90)		
C ₅		R ₃ SiH, EtI, Et ₂ NH, [RuCl ₂ (CO) ₃] ₂ , MeC ₆ H ₅ , 100°, 16 h		(—)	R ₃ = Et ₃ , <i>t</i> -BuMe ₂ , Me ₂ Ph
		PhSiH ₃ (1.2 eq), Mn(CO) ₅ PPh ₃ Ac, (3.0 mol %), C ₆ D ₆ , rt, 30 min	EtOPr- <i>i</i>	(95)	
		PhSiH ₃ (1.2 eq), Mn(CO) ₅ PPh ₃ Ac, (3.0 mol %), C ₆ D ₆ , rt, 30 min		(40)	
		 1. OEt, SbCl ₅ , TMSCl, SnI ₂ , CH ₂ Cl ₂ , -78°, 30 min 2. Et ₃ SiH (1.5 eq), -23°, 2.5 h	 I	(91)	
		 1. OEt, TlSbCl ₆ (5-30 mol %), CH ₂ Cl ₂ , -78°, 30 min 2. Et ₃ SiH (1.5 eq), -23°, 2.5 h	I	(95)	
					306
					306

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.																				
	OTBS 1. $OEt, SbCl_5, TMSCl, SnI_2, CH_2Cl_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$	 (71) cis:trans = 36:64	306																				
	OTBS 1. $OEt, TrSbCl_6$ (5-30 mol%), $CH_2Cl_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$	I (56) cis:trans = 31:69	306																				
	OTBS 1. $OEt, SbCl_5, TMSCl, SnI_2, CH_2Cl_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$	 (56) cis:trans = 31:69	306																				
	OTBS 1. $OEt, TrSbCl_6$ (5-30 mol%), $CH_2Cl_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$	I (56) cis:trans = 31:69	306																				
C_{5-20} 	Et_3SiH (1 eq), $ZnCl_2$, heat, 3-4 h	RCH_2-O-CH_2R <table><tr><th>R</th><th></th></tr><tr><td>Et</td><td>(70)</td></tr><tr><td><i>n</i>-Pr</td><td>(76)</td></tr><tr><td><i>i</i>-Bu</td><td>(82)</td></tr><tr><td><i>n</i>-Bu</td><td>(72)</td></tr><tr><td><i>n</i>-C₅H₁₁</td><td>(69)</td></tr><tr><td><i>n</i>-C₁₅H₃₁</td><td>(64)</td></tr><tr><td><i>n</i>-C₁₇H₃₅</td><td>(70)</td></tr><tr><td>Ph</td><td>(60)</td></tr><tr><td>4-BrC₆H₄</td><td>(56)</td></tr></table>	R		Et	(70)	<i>n</i> -Pr	(76)	<i>i</i> -Bu	(82)	<i>n</i> -Bu	(72)	<i>n</i> -C ₅ H ₁₁	(69)	<i>n</i> -C ₁₅ H ₃₁	(64)	<i>n</i> -C ₁₇ H ₃₅	(70)	Ph	(60)	4-BrC ₆ H ₄	(56)	298
R																							
Et	(70)																						
<i>n</i> -Pr	(76)																						
<i>i</i> -Bu	(82)																						
<i>n</i> -Bu	(72)																						
<i>n</i> -C ₅ H ₁₁	(69)																						
<i>n</i> -C ₁₅ H ₃₁	(64)																						
<i>n</i> -C ₁₇ H ₃₅	(70)																						
Ph	(60)																						
4-BrC ₆ H ₄	(56)																						

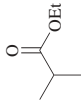
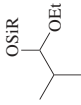

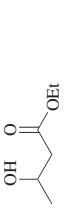

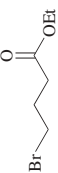
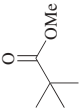


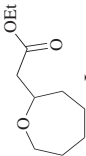

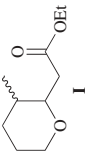
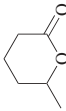
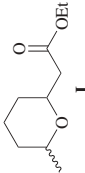
C ₆		R ₃ SiH (1.5 eq), catalyst, MeC ₆ H ₅ , 100°, 16 h		299
		R ₃ Catalyst		
		Et ₃ Ru ₃ (CO) ₁₂	(78)	
		Et ₃ [RuCl ₂ (CO) ₃] ₂	(86)	
		<i>i</i> -BuMe ₂ Ru ₃ (CO) ₁₂	(79)	
		<i>i</i> -BuMe ₂ [RuCl ₂ (CO) ₃] ₂	(87)	
		PhMe ₂ Ru ₃ (CO) ₁₂	(87)	
		PhMe ₂ [RuCl ₂ (CO) ₃] ₂	(72)	
		PhSiH ₃ (1.2 eq), Mn(CO) ₅ Br (1.5-3.0 mol%), C ₆ D ₆ , rt, 30 min		295
		(MeO) ₃ SiH (3.0 eq), LiOMe (6 mol%), THF, 65°, 0.5 h	(100)	294
		(MeO) ₃ SiH (3.5 eq), LiOMe (6 mol%), THF, 65°, 0.5 h	(80)	294
		PhSiH ₃ (1.2 eq), Mn(CO) ₅ Br (1.5-3.0 mol%), C ₆ D ₆ , rt, 35 min	(72)	295
		PhSiH ₃ (1.2 eq), Mn(CO) ₅ Br (1.5-3.0 mol%), C ₆ D ₆ , rt, 30 min	(10)	295
		PhSiH ₃ (1.2 eq), Mn(CO) ₅ Br (1.5-3.0 mol%), C ₆ D ₆ , rt, 12 h	I (10)	295
		PhSiH ₃ (1.2 eq), Mn(CO) ₅ Br (1.5-3.0 mol%), C ₆ D ₆ , rt, 30 min	(65)	295

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>OTBS</p> <p>1. $\text{OEt}, \text{SbCl}_5, \text{TMSCl}, \text{SnI}_2$ $\text{CH}_2\text{Cl}_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$</p> <p>OTBS</p> <p>1. $\text{OEt}, \text{TrSbCl}_6$ (5-30 mol%), $\text{CH}_2\text{Cl}_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$</p>	<p> (87)</p> <p>I (90)</p>	306
	<p>OTBS</p> <p>1. $\text{OEt}, \text{SbCl}_5, \text{TMSCl}, \text{SnI}_2$ $\text{CH}_2\text{Cl}_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$</p> <p>OTBS</p> <p>1. $\text{OEt}, \text{TrSbCl}_6$ (5-30 mol%), $\text{CH}_2\text{Cl}_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$</p>	<p> (84) cis:trans = 12:88</p> <p>I (83) cis:trans = 10:90</p>	306
	<p>OTBS</p> <p>1. $\text{OEt}, \text{SbCl}_5, \text{TMSCl}, \text{SnI}_2$ $\text{CH}_2\text{Cl}_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$</p> <p>OTBS</p> <p>1. $\text{OEt}, \text{TrSbCl}_6$ (5-30 mol%), $\text{CH}_2\text{Cl}_2, -78^\circ, 30 \text{ min}$ 2. Et_3SiH (1.5 eq), $-23^\circ, 2.5 \text{ h}$</p>	<p> (79) cis:trans > 99:1</p> <p>I (82) cis:trans > 99:1</p>	306

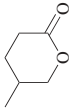
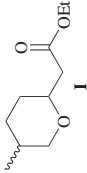

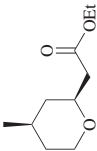

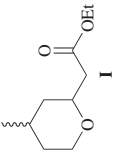
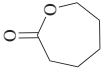

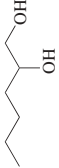
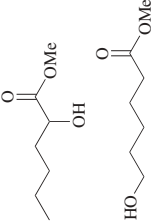

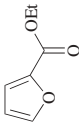


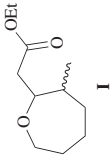
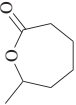
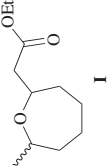


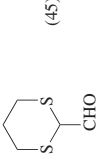
	1. OTBS OEt , SbCl_5 , TMSCl , SnI_2 , CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h		(87) cis:trans = 7:93	306
	OTBS 1. OEt , TrSbCl_6 (5-30 mol%), CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h	I (82) cis:trans = 4:96		306
	OTBS Et_3SiH , OEt , SbCl_3 , TMSCl , SnI_2 , CH_2Cl_2		(84)	306
	OTBS 1. OEt , SbCl_5 , TMSCl , SnI_2 , CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h		(82) cis:trans > 99:1	306
	OTBS 1. OEt , TrSbCl_6 (5-30 mol%), CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h	I (89) cis:trans > 99:1		306
	$(\text{EtO})_3\text{SiH}$ (2.2 eq), CsF (1 eq), rt, 1 min		(50)	81
C_7	$(\text{MeO})_3\text{SiH}$ (3.5 eq), LiOMe (6 mol%), THF , 65° , 9.5 h		(100)	294
	$(\text{MeO})_3\text{SiH}$ (3.5 eq), LiOMe (6 mol%), THF , 65° , 0.5 h		(63)	294

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Cp_2TiCl_2 (5 mol%), $n\text{-BuLi}$ (10 mol%), THF, -15° , 15 min 2. $(\text{EtO})_3\text{SiH}$ (2 eq), ester addition, rt, 0.5–2 h	 (75)	290
	OTBS 1. OEt , SbCl_5 , TMSCl , SnI_2 , CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h	 (91) cis:trans > 99:1	306
	OTBS 1. OEt , TrtSbCl_6 (5–30 mol%), CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h	I (86) cis:trans > 99:1	306
	OTBS 1. OEt , SbCl_5 , TMSCl , SnI_2 , CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h	 (85) cis:trans > 99:1	306
	OTBS 1. OEt , TrtSbCl_6 (5–30 mol%), CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h	I (81) cis:trans > 99:1	306
	Ph_3SiH , $(\text{C}_6\text{F}_5)_3\text{B}$ (1 mol%), MeC_6H_5 , rt	 (45)	116

C_{7:9}

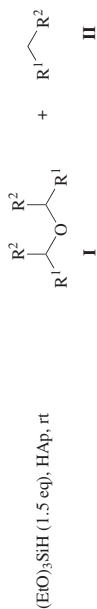


353

C_{7:28}



81



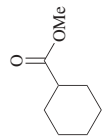
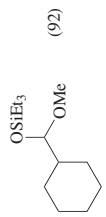
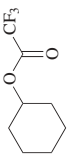

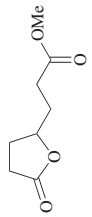
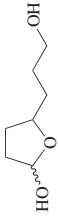
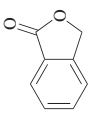
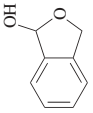
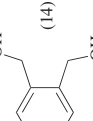
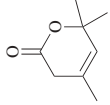
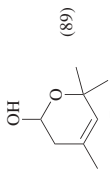





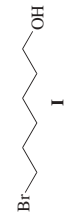
R ¹	R ²	Time
<i>n</i> -C ₅ H ₁₁	MeO	24 h (44)
Ph	EtO	20 h (97)




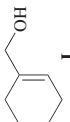
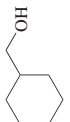
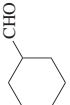


R₃SiH (x eq), CsF (1 eq)

R ¹	R ²	R ₃ Si	x	Temp	Time
<i>n</i> -C ₄ H ₉	Et	Ph ₂ HSi	1.1	140°	4 h (90)
<i>n</i> -C ₄ H ₉	Et	(EtO) ₂ MeSi	2.2	120°	3 h (90)
<i>n</i> -C ₄ H ₉	Et	(EtO) ₃ Si	2.2	rt	1 min (90)
Ph	Et	Ph ₂ HSi	1.1	140°	4 h (65)
Ph	Et	(EtO) ₃ Si	2.2	100°	3 h (65)
MeO ₂ C(CH ₂) ₇	Me	Ph ₂ HSi	1.1	140°	4 h (65)
MeO ₂ C(CH ₂) ₇	Me	(EtO) ₂ MeSi	2.2	120°	2 h (65)
MeO ₂ C(CH ₂) ₇	Me	(EtO) ₃ Si	2.2	rt	12 h (65)
<i>n</i> -C ₁₁ H ₂₃	Et	(EtO) ₂ MeSi	2.2	100°	20 h (90)
<i>n</i> -C ₁₁ H ₂₃	Et	(EtO) ₃ Si	2.2	60°	0.5 h (90)
H ₂ C=CH(CH ₂) ₈	Me	Ph ₂ HSi	1.1	140°	10 h (70)
H ₂ C=CH(CH ₂) ₈	Me	(EtO) ₂ MeSi	2.2	80°	48 h (65)
H ₂ C=CH(CH ₂) ₈	Me	(EtO) ₃ Si	2.2	rt	20 h (65)
H ₂ C=CH(CH ₂) ₈	Me	(EtO) ₃ Si	2.2	60°	0.5 h (70)
<i>n</i> -C ₈ H ₁₇ CH=CH(CH ₂) ₇	Me	Ph ₂ HSi	1.1	140°	4 h (70)
<i>n</i> -C ₈ H ₁₇ CH=CH(CH ₂) ₇	Me	(EtO) ₂ MeSi	2.2	120°	3 h (85)
<i>n</i> -C ₈ H ₁₇ CH=CH(CH ₂) ₇	Me	(EtO) ₃ Si	2.2	rt	4 h (90)
H ₂ C=CH(CH ₂) ₈	menthyl	(EtO) ₃ Si	2.2	rt	72 h (75)
H ₂ C=CH(CH ₂) ₈	menthyl	(EtO) ₃ Si	2.2	60°	9 h (75)
<i>n</i> -C ₈ H ₁₇ CH=CH(CH ₂) ₇	menthyl	(EtO) ₃ Si	2.2	rt	72 h (80)

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₈	Et ₃ SiH, EtI, Et ₂ NH, [RuCl ₂ (CO) ₂] ₂ , MeC ₆ H ₅ , 100°, 16 h	 (92)	299
	EtCl ₂ SiH (2 eq), AlBr ₃ (1 eq), 20°, 2 h	 (69)	192
	PMHS (5 eq), Cp ₂ TiF ₂ (2 mol%), TBAF/alumina (1 mol%), MeC ₆ H ₅ , rt	 (88)	301
	PMHS (5 eq), Cp ₂ Ti(OC ₆ H ₄ Cl-4) ₂ (2 mol%), TBAF/alumina (1 mol%), MeC ₆ H ₅ , rt	 (75) +  (14)	302
	PMHS (5 eq), Cp ₂ Ti(OC ₆ H ₄ Cl-4) ₂ (2 mol%), TBAF/alumina (1 mol%), MeC ₆ H ₅ , rt	 (89)	301, 302
	PMHS (5 eq), Cp ₂ TiF ₂ (2 mol%), TBAF/alumina (1 mol%), MeC ₆ H ₅ , rt	 (78)	301
	1. Cp ₂ TiCl ₂ (5 mol%), <i>n</i> -BuLi (10 mol%), THF, -15°, 15 min 2. (EtO) ₃ SiH (3.3 eq), ester addition, rt, 0.5-2 h	 (78)	290
	1. Cp ₂ TiCl ₂ (5 mol%), <i>n</i> -BuLi (10 mol%), THF, -15°, 15 min 2. (EtO) ₃ SiH (2 eq), ester addition, -20° to rt, 8 h	 (78)	290

PMHS (5 eq), Cp_2TiCl_2 (15 mol%), EtMgBr (2 eq), THF, rt, 3 h	I (53) + 	(6)	289
$(\text{EtO})_3\text{SiH}$ (2.5 eq), $\text{Ti}(\text{OPr-}i)_4$, (5 mol%), 40–55°, 6 h	I (75)		291
Ph_3SiH , $(\text{C}_6\text{F}_5)_3\text{B}$ (1 mol%), MeC_6H_5 , rt		(70)	116
1. EtMe_2SiH (4 eq), 223 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add ester, 2 h	I (47) + 	(40)	280
PMHS (2.5 eq), Cp_2TiCl_2 , <i>n</i> -BuLi (2 eq, 5 mol%), THF, rt, 1 h	 I	(65)	289
1. Cp_2TiCl_2 (5 mol%), <i>n</i> -BuLi (10 mol%), THF, –15°, 15 min 2. $(\text{EtO})_3\text{SiH}$ (2 eq), ester addition, rt, 0.5–2 h	I (71)		290
$(\text{EtO})_3\text{SiH}$ (2.5 eq), $\text{Ti}(\text{OPr-}i)_4$ (5 mol%), 40–55°, 16 h		(88)	291
Et_3SiH (1.5 eq), $[\text{RuCl}_2(\text{CO})_3]_2$, EtI, Et_2NH , MeC_6H_5 , 100°, 16 h		(90)	299

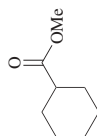
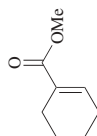
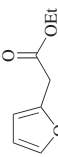
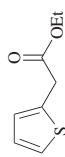

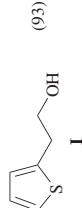
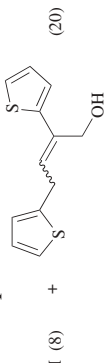
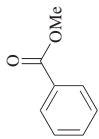
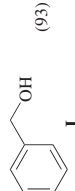
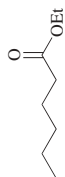


TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
 	PMHS (2.5 eq), Cp ₂ TiCl ₂ (5 mol%), EtMgBr (2 eq), THF, rt, 17.5 h	 (75)	289
	(EtO) ₃ SiH (2.5 eq), Ti(OPr- <i>i</i>) ₄ (5 mol%), 40-55°, 22 h	 (93) I	291
	PMHS (2.5 eq), Ti(OPr- <i>i</i>) ₄ (25 mol%), 65°, 24 h	 (20) I (8) +	292
	1. Cp ₂ TiCl ₂ (5 mol%), <i>n</i> -BuLi (10 mol%), THF, -15°, 15 min 2. (EtO) ₃ SiH (2 eq), ester addition, rt, 0.5-2 h	I (88)	290
	PMHS (2.5 eq), Cp ₂ TiCl ₂ (5 mol%), EtMgBr (2 eq), THF, rt, 17.5 h	I (92)	289
	1. Cp ₂ TiCl ₂ (5 mol%), <i>n</i> -BuLi (10 mol%), THF, -15°, 15 min 2. (EtO) ₃ SiH (2 eq), ester addition, rt, 0.5-2 h	 (93) I	290
	(EtO) ₃ SiH (2.5 eq), PhSiH ₃ (1.4 eq), Ti(OPr- <i>i</i>) ₄ (5 mol%), 40-55°, 16 h	I (75)	291
	PMHS (2.5 eq), Cp ₂ TiCl ₂ (2 mol%), EtMgBr (2 eq), THF, rt, 1.5 h	I (94)	289
	1. EtMe ₂ SiH (4 eq), 223 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add ester, 24 h	I (52)	280

PMHS (xs), zinc catalyst (0.2 eq),
additive, (*i*-Pr)₂O, 70°, 4 h

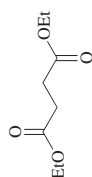
Zinc catalyst	Additive	
Zn(EH) ₂	NaBH ₄ (1eq)	(100)
Zn(O ₂ CC ₆ H ₅) ₂	NaBH ₄ (1 eq)	(96)
Zn(OAc) ₂	NaBH ₄ (1 eq)	(2)
Zn(EH) ₂	MeMgCl (1 eq)	(100)
Zn(EH) ₂	AlEt ₃ (2 eq)	(8)
Zn(EH) ₂	BH ₃ (1 eq)	(62)
Zn(EH) ₂	AlH(Bu- <i>i</i>) ₂ (1 eq)	(66)
ZnI ₂	LiH	(78)
ZnCl ₂	LiAlH ₄	(13)
ZnEt ₂	Me ₂ N(CH ₂) ₂ OH (1 eq)	(13)
ZnEt ₂	H ₂ N(CH ₂) ₂ NH ₂ (1 eq)	(84)
ZnEt ₂	Me ₂ N(CH ₂) ₂ NMe ₂ (1 eq)	(84)



PhSiH₃ (1.2 eq), Mn(CO)₅Br
(1.5-3.0 mol%), C₆D₆, rt, 30 min



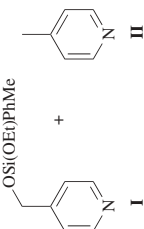
295



PhSiH₃ (1.2 eq), Mn(CO)₅Br
(1.5-3.0 mol%), C₆D₆, rt, 20 min



295



PhMeSiH₂ (1.5 eq),
Cp₂TiMe₂ (10 mol%), 80°, 39 h

I + II (90), I:II = 4:1

264

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

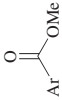

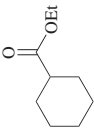
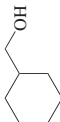
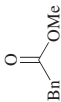
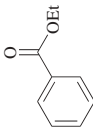
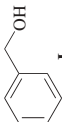
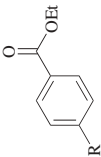
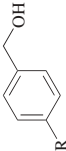
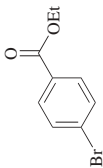
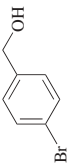

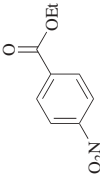
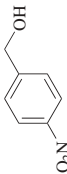
Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₈₋₁₁</div> <div>  </div>	<div> <div>Ar</div> <div>Ph</div> <div>4-BrC₆H₄</div> <div>4-ClC₆H₄</div> <div>2,4-Cl₂C₆H₃</div> <div>3,5-Cl₂C₆H₃</div> <div>3-MeC₆H₄</div> <div>4-MeC₆H₄</div> <div>2,4-Me₂C₆H₃</div> <div>3,4,5-(MeO)₃C₆H₂</div> </div>	<div> <div>Ar-CH₂-OH</div> <div>(95)</div> <div>(96)</div> <div>(97)</div> <div>(94)</div> <div>(83)</div> <div>(90)</div> <div>(93)</div> <div>(93)</div> <div>(81)</div> </div>	<div> <div>278</div> </div>
<div>C₈₋₁₄</div> <div>  </div>	<div> <div>PMHS (3 eq), TBAF (2 mol%), THF, rt</div> <div>PMHS (2.5 eq), Ti(OPr-<i>i</i>)₄ (x mol%)</div> </div>	<div> <div>R¹-CH₂-OH</div> <div></div> </div>	<div> <div>292</div> </div>

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 	PMHS (2.5 eq), Cp ₂ TiCl ₂ (5 mol%), EtMgBr (2 eq), THF, rt, 5 h	 (88)	289
	PMHS (3 eq), TBAF (2 mol%), THF, rt	Bn-CH ₂ -OH (76)	278
	PMHS (1.2 eq), KF•2H ₂ O (1.3 eq), DMSO, 80°, 6.5 h	 I (81)	82, 83
	[HSi(OEt) ₄] ₂ K, THF, rt, 8-15 h	I (86)	288
	(EtO) ₃ SiH (2.3 eq), CsF (1 eq), 60°, 30 min	I (90)	83
	1. Cp ₂ TiCl ₂ (5 mol%), <i>n</i> -BuLi (10 mol%), THF, -15°, 15 min 2. (EtO) ₃ SiH (3.3 eq), ester addition, rt, 0.5-2 h	 (88) <div style="display: flex; align-items: center; justify-content: center;"><div style="text-align: center; margin-right: 10px;">$\frac{R}{OH}$ (88)</div><div style="text-align: center; margin-right: 10px;">$\frac{R}{NH_2}$ (81)</div></div>	290
	PMHS (2.5 eq), Cp ₂ TiCl ₂ (15 mol%), EtMgBr (2 eq), THF, rt, 3 h	 (40) +  (9)	289
	(EtO) ₃ SiH (1.3 eq), PhSiH ₃ (1.4 eq), Ti(OPr- <i>i</i>) ₄ (5 mol%), 40-55°, 20 h	 (75)	291

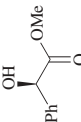
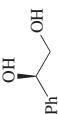
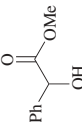
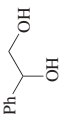
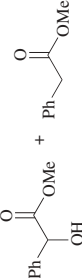

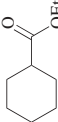
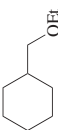
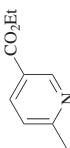

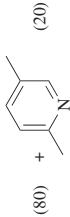
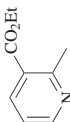
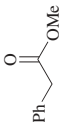

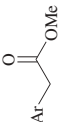
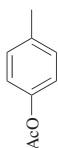
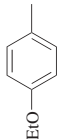
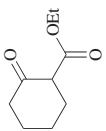
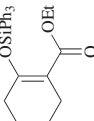
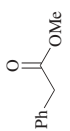






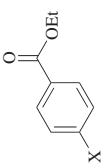
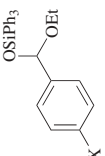

		PMHS (3 eq), TBAF (2 mol%), THF, rt	(90) >95% ee	278
		(MeO) ₃ SiH (3.5 eq), LiOMe (6 mol%), THF, 65°, 9.5 h	(94)	294
	I	(MeO) ₃ SiH (3.5 eq), LiOMe (6 mol%), THF, 65°, 9.5 h	I (78) +  (—)	294
		PhSiH ₃ (1.2 eq), Mn(CO) ₅ Br (1.5–3.0 mol%), C ₆ D ₆ , rt, 25 min	(70)	295
		PhMeSiH ₂ (1.5 eq), Cp ₂ TiMe ₂ (10 mol%), rt, 24 h	(80) +  (20)	264
	I	PhMeSiH ₂ (1.5 eq), Cp ₂ TiMe ₂ (10 mol%), 6 d	I + II (100), I:II = 3:2	264
		PhSiH ₃ (1.2 eq), Mn(CO) ₄ PPh ₃ Ac (3.0 mol%), C ₆ D ₆ , rt, 30 min	(83)	295
	Ar	Et ₃ SiH (5.0 eq), TiCl ₄ (1.5 eq), TMSOTf (3.1 eq), CH ₂ Cl ₂ , rt, 20 h	Ar Ph (40) 4-BrC ₆ H ₄ (80) 4-O ₂ NC ₆ H ₄ (72)	297
		PhSiH ₃ (1.2 eq), Mn(CO) ₄ PPh ₃ Ac (3.0 mol%), C ₆ D ₆ , rt, 12 h	(12)	295

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 	Ph ₃ SiH, (C ₆ F ₅) ₃ B (2 mol%), MeC ₆ H ₅ , rt	 (78) ^b	116
	Et ₃ SiH (1.5 eq), [RuCl ₂ (CO) ₃] ₂ , EtI, Et ₂ NH, MeC ₆ H ₅ , 100°, 16 h	Ph-CH ₂ -CHO (65)	299
	Ph ₃ SiH, (C ₆ F ₅) ₃ B (2 mol%), MeC ₆ H ₅ , rt	 (80) ^c	116
	Et ₃ SiH (2-3 eq), Pd/C (2-5 mol%), acetone, rt, 30-60 min	 (91)	300
	Et ₃ SiH (2-3 eq), Pd/C (2-5 mol%), acetone, rt, 30-60 min	 (75)	300
C _{9,10} 	Ph ₃ SiH (1 eq), (C ₆ F ₅) ₃ B (2 mol%)	 X = H (80) X = Me, Cl, NO ₂ (—)	115
C _{9,15} 	Ph ₃ SiH ₂ (3 eq), catalyst (1.25 mol%), PPh ₃ (5 eq), THF, rt	R ¹ -CH ₂ -OH	293

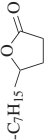
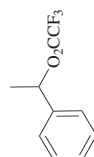
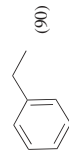
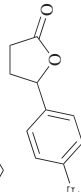
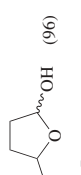
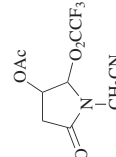

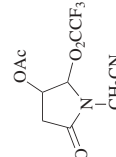
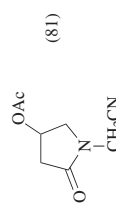

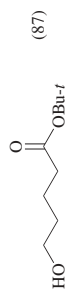
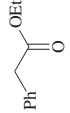
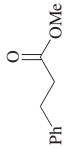
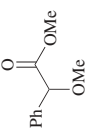
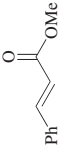

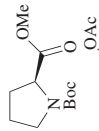
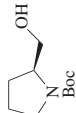
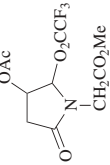
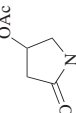
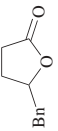
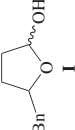


R ¹	R ²	Catalyst	Time		
Ph	Et	[RhCl(cod)] ₂	144 h	(70)	193
Ph	Et	RhCl(PPh ₃) ₃	24 h	(56)	301, 302
Br(CH ₂) ₆	Et	[RhCl(cod)] ₂	72 h	(92)	301
Br(CH ₂) ₆	Et	RhCl(PPh ₃) ₃	24 h	(92)	739
Bn	Et	[RhCl(cod)] ₂	72 h	(92)	290
Me	<i>n</i> -C ₁₀ H ₂₁	[RhCl(cod)] ₂	72 h	(94)	
<i>n</i> -C ₉ H ₁₉	Et	[RhCl(cod)] ₂	72 h	(98)	
<i>n</i> -C ₉ H ₁₉	<i>i</i> -Bu	[RhCl(cod)] ₂	72 h	(92)	
<i>n</i> -C ₉ H ₁₉	<i>i</i> -Bu	RhCl(PPh ₃) ₃	6 h	(95)	
<i>n</i> -C ₁₁ H ₂₃	<i>i</i> -Pr	[RhCl(cod)] ₂	72 h	(66)	
<i>n</i> -C ₁₁ H ₂₃	<i>i</i> -Pr	RhCl(PPh ₃) ₃	6 h	(80)	
<i>n</i> -C ₇ H ₁₅		[RhCl(cod)] ₂	72 h	(63)	
		Ph ₃ SiH, O ₂ NC ₆ H ₅ , 80°, 13 h		 (90)	
		PMHS (5 eq), Cp ₂ Ti(OC ₄ H ₄ Cl-4) ₂ (2 mol%), TBAF/alumina (1 mol%), MeC ₆ H ₅ , rt		 (96)	
		PMHS (5 eq), Cp ₂ TiF ₂ (2 mol%), TBAF/alumina (1 mol%), MeC ₆ H ₅ , rt		 (97)	
		Et ₃ SiH (1.2 eq), TFA (13 eq), rt, 1 h		 (81)	
		1. Cp ₂ TiCl ₂ (5 mol%), <i>n</i> -BuLi (10 mol%), THF, -15°, 15 min 2. (EtO) ₃ SiH (2 eq), ester addition, -20° to rt, 8 h		 (87)	

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	(EtO) ₃ SiH (2.5-3.0 eq), Ti(OPr-i) ₄ (5 mol%), 40-55°, 10 h	Ph-CH ₂ -CH ₂ -OH (89)	291
	1. EtMe ₂ SiH (2.4 eq), 223 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add ester, 0.5 h	Ph-CH ₂ -CH ₂ -CH ₂ -OH (97)	280
	(MeO) ₃ SiH (3.5 eq), LiOMe (6 mol%), THF, 65°, 9.5 h	Ph-CH(OMe)-CH ₂ -OH (76)	294
	PMHS (3 eq), TBAF (2 mol%), THF, rt	Ph-CH=CH-CH ₂ -OH (84)	278
C ₁₀₋₁₁ 	Et ₃ SiH (5.0 eq), TiCl ₄ (1.5 eq), TMSOTf (3.1 eq), CH ₂ Cl ₂ , rt, 20 h	Ar-CH ₂ -CH ₂ -OMe Ar Ph (75) 4-MeOC ₆ H ₄ (89)	297
C ₁₁ 	PMHS (2.5 eq), Cp ₂ TiCl ₂ (5 mol%), EtMgBr (2 eq), THF, rt, 23 h	 (70)	289
	Et ₃ SiH (1.2 eq), TFA (13 eq), rt, 1 h	 (80)	739
	PMHS (5 eq), Cp ₂ Ti(OC ₆ H ₄ Cl-4) ₂ (2 mol%), TBAF/alumina (1 mol%), MeC ₆ H ₅ , rt	 (93)	301, 302
	PMHS (5 eq), Cp ₂ TiF ₂ (2 mol%), TBAF/alumina (1 mol%), MeC ₆ H ₅ , rt	 (87)	301

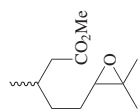

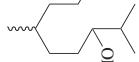

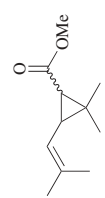
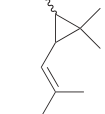


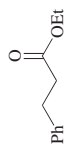
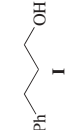






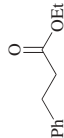



				289
	PMHS (2.5 eq), Cp_2TiCl_2 (5 mol%), EtMgBr (2 eq), THF, -78° to rt, 1.5 h	(44) +	(28)	
				292
	PMHS (2.5 eq), $\text{Ti}(\text{OPr-}i\text{)}_4$ (100 mol%), 65° , 8 h	(58)		
				290
	1. Cp_2TiCl_2 (5 mol%), <i>n</i> -BuLi (10 mol%), THF, -15° , 15 min 2. $(\text{EtO})_3\text{SiH}$ (1.2 eq), ester addition, -20° to rt, 8 h	I (94)	(82)	
				289
	PMHS (2.5 eq), Cp_2TiCl_2 (5 mol%), EtMgBr (2 eq), THF, rt, 23 h	I (55) +	II (11)	280
	1. EtMe_2SiH (2.4 eq), 2 (1 mol%), 1,4-dioxane, 20° , 0.5 h 2. Add ester, 1 h			

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

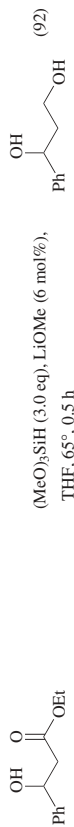
Ester	Conditions	Product(s) and Yield(s) (%)	Refs.		
<div>C₁₁</div> <div></div>	1. R ₃ SiH (2.4 eq), 223 (1 mol%), solvent 2. Add ester	<div> I</div> <div> II</div> <div> III</div>	280		
R ₃ Si	Solvent	Temp	Time	% Conversion	I:II:III
EtMe ₂ Si	1,4-dioxane	20°	1 h	(100)	20:0:80
HMe ₂ Si(CH ₂) ₂ (Me) ₂ Si	1,4-dioxane	20°	2 h	(100)	16:0:84
Et ₃ MeSi	1,4-dioxane	20°	5 h	(100)	76:0:24
PhMe ₂ Si	1,4-dioxane	20°	21 h	(95)	17:0:83
Ph ₂ MeSi	1,4-dioxane	20°	21 h	(74)	16:0:84
Et ₃ Si	1,4-dioxane	20°	21 h	(7)	0:100:0
(<i>i</i> -Pr) ₃ Si	1,4-dioxane	20°	24 h	(0)	0:0:0
EtMe ₂ Si	C ₆ H ₆	20°	1 h	(100)	42:0:58
EtMe ₂ Si	Et ₂ O	20°	2 h	(100)	45:16:39
EtMe ₂ Si	tetrahydropyran	20°	2 h	(94)	53:0:47
EtMe ₂ Si	oxepane	20°	8 h	(69)	61:0:39
EtMe ₂ Si	C ₃ H ₅ N	20°	22 h	(0)	0:0:0
EtMe ₂ Si	1,4-dioxane	10°	1 h	(100)	28:0:72
1. EtMe ₂ SiH (2.4 eq), 224 (1 mol%) 2. Add ester	I (56)				280

280

1. EtMe₂SiH (2.4 eq), **225** (1 mol%), **I** (34) + **II** (0.3)
2. Add ester 280

1. EtMe₂SiH (2.4 eq), **226** (1 mol%), **I** (40) + **II** (0.8)
2. Add ester 280

1. Et₂MeSiH (2.4 eq), **223** (1 mol%), **I** (87)
THP, 20°, 0.5 h
2. Add ester, 1 h 280

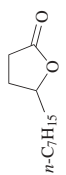
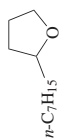
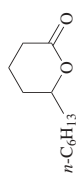
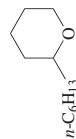
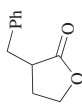
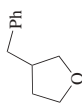


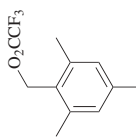
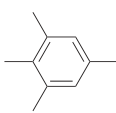


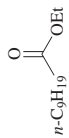
(MeO)₃SiH (3.0 eq), LiOMe (6 mol%),
THF, 65°, 0.5 h 294

Et₃SiH (x eq), TiCl₄ (y eq),
co-catalyst (z eq), CH₂Cl₂, rt, 20 h 297

x	y	Co-catalyst	z
5.0	3.0	None	— (27)
5.0	1.5	TMSOTf	3.0 (81)
5.0	—	TMSOTf	3.0 (—)
5.0	1.5	AgOTf	3.0 (63)
5.0	1.5	AgOTf, TMSCl	3.0, 3.0 (76)

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.														
C ₁₁  <i>n</i> -C ₇ H ₁₅	1. EtMe ₂ SiH (4 eq), 223 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add ester, 3 h	 <i>n</i> -C ₇ H ₁₅ (79)	280														
 <i>n</i> -C ₆ H ₁₃	1. EtMe ₂ SiH (4 eq), 223 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add ester, 2 h	 <i>n</i> -C ₆ H ₁₃ (73)	280														
	Et ₃ SiH (5.0 eq), TiCl ₄ (1.5 eq), TMSOTf (3.1 eq), CH ₂ Cl ₂ , rt, 20 h	 (67)	297														
C ₁₁₋₁₆ 	Et ₃ SiH (5.0 eq), TiCl ₄ (1.5 eq), TMSOTf (3.1 eq), CH ₂ Cl ₂ , rt, 20 h	 Ph-CH ₂ -CH ₂ -CH ₂ -CH ₂ -OR <table><tr><th>R</th><th></th></tr><tr><td>Me</td><td>(81)</td></tr><tr><td>Et</td><td>(78)</td></tr><tr><td><i>i</i>-Pr</td><td>(39)</td></tr><tr><td><i>n</i>-Bu</td><td>(79)</td></tr><tr><td><i>c</i>-C₆H₁₁</td><td>(34)</td></tr><tr><td>Ph</td><td>(67)</td></tr></table>	R		Me	(81)	Et	(78)	<i>i</i> -Pr	(39)	<i>n</i> -Bu	(79)	<i>c</i> -C ₆ H ₁₁	(34)	Ph	(67)	297
R																	
Me	(81)																
Et	(78)																
<i>i</i> -Pr	(39)																
<i>n</i> -Bu	(79)																
<i>c</i> -C ₆ H ₁₁	(34)																
Ph	(67)																
C ₁₂ 	Ph ₂ SiH ₂ , O ₂ NC ₆ H ₅ , 80°, 7 h	 (90)	193														



293

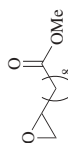


x	y	Time	
4	5.0	72 h	(96)
4	2.5	72 h	(92)
4	1.0	72 h	(40)
3	2.5	72 h	(98)
2	2.5	72 h	(72)
3	2.5	6 h	(96)
3	1.0	6 h	(51)
3	1.0	24 h	(56)

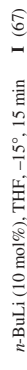
292



Silane	Catalyst	x	Temp	Time
PMHS	Ti(OPr- <i>i</i>) ₄	25	65	24 h (100)
PMHS	Ti(OPr- <i>i</i>) ₄	100	23	25 h (100)
PMHS	Ti(OPr- <i>i</i>) ₄	25	65	2 h (100)
Ph ₂ SiH ₂	Ti(OPr- <i>i</i>) ₄	25	65	25 h (100)
Cl ₃ SiH	Ti(OPr- <i>i</i>) ₄	100	23	24 h (0)
PMHS	Ti(OBu- <i>n</i>) ₄	25	65	24 h (75)
PMHS	Ti(OBu- <i>n</i>) ₄	100	65	2 h (90)
Ph ₂ SiH ₂	THEATi(OPr- <i>i</i>)	100	23	96 h (0)



292



290

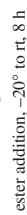
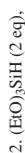
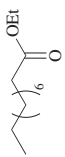
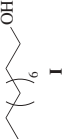

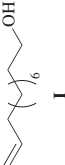
















TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	(EtO) ₃ SiH (2.5-3.0 eq), Ti(OPr- <i>i</i>) ₄ (5 mol%), 40-55°, 10 h	 I (69)	291
	Ph ₃ SiH, (C ₆ F ₅) ₃ B (1 mol%), MeC ₆ H ₅ , rt	 I (87)	116
	(EtO) ₃ SiH (2.5-3.0 eq), Ti(OPr- <i>i</i>) ₄ (5 mol%), 40-55°, 16 h	 I (95)	291
	PMHS (3 eq), TBAF (2 mol%), THF, rt	 I (83)	278
	(EtO) ₃ SiH (2.5-3.0 eq), Ti(OPr- <i>i</i>) ₄ (5 mol%), 40-55°, 21 h	 I (70)	291
	(EtO) ₃ SiH (2.5-3.0 eq), Ti(OPr- <i>i</i>) ₄ (5 mol%), 40-55°, 18 h	 I (80)	291
	1. (EBTHD) ₂ TiCl ₂ (5 mol%), <i>n</i> -BuLi (10 mol%), THF, -15°, 15 min 2. (EtO) ₃ SiH (2 eq), ester addition, -20° to rt, 8 h	 I (83)	290
	PMHS (2.5 eq), Cp ₂ TiCl ₂ (5 mol%), EtMgBr (2 eq), THF, rt, 1 h	 I (91)	289
	PMHS (10 eq), Ti(OPr- <i>i</i>) ₄ (1 eq), THF	 I (89)	279

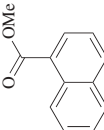
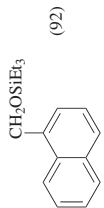
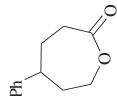
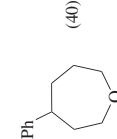
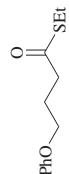
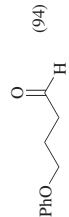
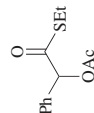
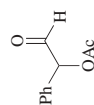
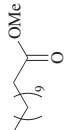
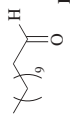
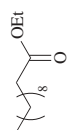

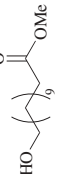
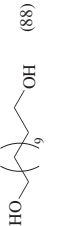


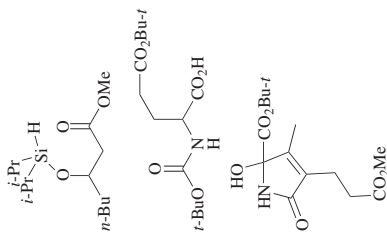
		Et_3SiH (3.3 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 20 h	282
		Et_3SiH (5.0 eq), TiCl_4 (1.5 eq), TMSOTf (3.1 eq), CH_2Cl_2 , rt, 20 h	297
		Et_3SiH (2-3 eq), Pd/C (2-5 mol%), acetone, rt, 30-60 min	300
		Et_3SiH (2-3 eq), Pd/C (2-5 mol%), acetone, rt, 30-60 min	300
		$(\text{EtO})_3\text{SiH}$, CsF , 60° , 0.5 h	83
		PMHS , $\text{KF}\cdot 2\text{H}_2\text{O}$, DMSO , 80° , 6 h	83
		$[\text{HSi}(\text{OEt})_4]\text{K}$, THF , rt, 8-15 h	288
		$(\text{EtO})_3\text{SiH}$ (2.5-3.0 eq), $\text{Ti}(\text{OPr}-i)_4$ (5 mol%), $40-55^\circ$, 10 h	291

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

C₁₄

TBAF (0.5 eq), AcOEt, rt, 15 min

(81)

303

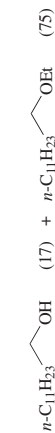
Et₃SiH (2.5 eq), TFA,
CH₂Cl₂, rt, 65 min(96) + Me₃CH (—)

307

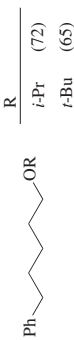
Et₃SiH (xs), TFA, 18°, 18 h, 45°, 3 h

(87)

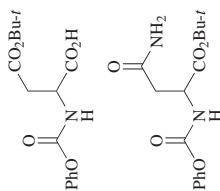
714

1. Et₃MeSiH (4 eq), **223** (1 mol%),
THP, 20°, 0.5 h
2. Add ester, 22 h

280

C_{14,15}Et₃SiH (5.0 eq), TiCl₄ (1.5 eq),
TMSOTf (3.1 eq), CH₂Cl₂, rt, 20 h

297

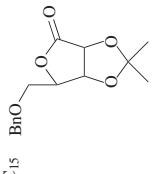
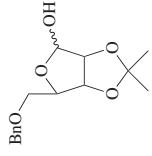
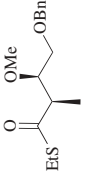
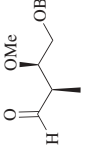
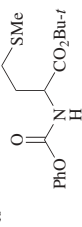
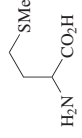
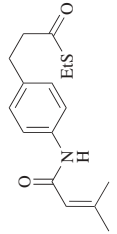
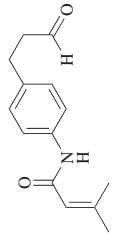
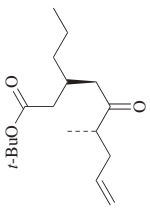
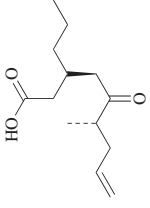
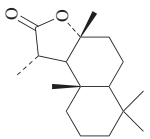
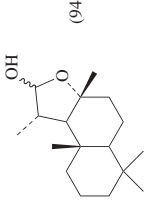
C₁₅Et₃SiH (2.5 eq), TFA,
CH₂Cl₂, rt, 45 min(100) + Me₃CH (—)

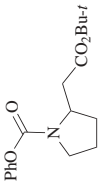
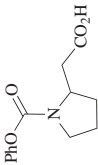
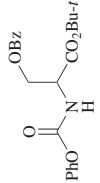
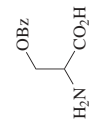
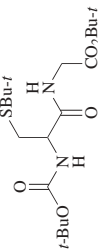
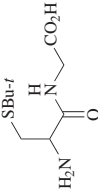
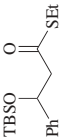
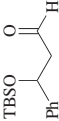
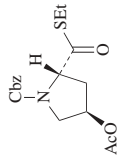
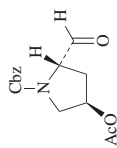
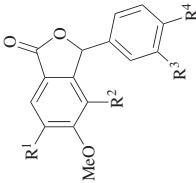
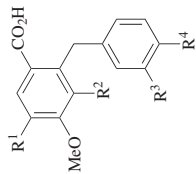
307

Et₃SiH (2.5 eq), TFA,
CH₂Cl₂, rt, 35 min(98) + Me₃CH (—)

307

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 	PMHS (5 eq), Cp ₂ Ti(OC ₆ H ₄ Cl-4) ₂ (2 mol %), TBAF/alumina (1 mol %), MeC ₆ H ₅ , rt	 (91)	302
	Et ₃ SiH, Pd/C	 (—)	740
C ₁₆ 	Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 25 min	 (95) + Me ₃ CH (—)	307
	Et ₃ SiH (2-3 eq), Pd/C (2-5 mol %), acetone, rt, 30-60 min	 (97)	300
C ₁₇ 	Et ₃ SiH, TFA, CH ₂ Cl ₂	 (100) + Me ₃ CH (—)	741
	PMHS (5 eq), Cp ₂ Ti(OC ₆ H ₄ Cl-4) ₂ (3 mol %), TBAF/alumina (1 mol %), MeC ₆ H ₅ , rt	 (94)	302

		Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 25 min	(90) + Me ₃ CH (—)	307																				
		Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 45 min	(100) + Me ₃ CH (—)	307																				
		Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 15 min	(100) + Me ₃ CH (—)	307																				
		Et ₃ SiH (2-3 eq), Pd/C (2-5 mol%), acetone, rt, 30-60 min	(88)	300																				
		Et ₃ SiH (2-3 eq), Pd/C (2-5 mol%), acetone, rt, 30-60 min	(88)	300																				
		Et ₃ SiH (3 eq), TFA (5 eq)	<table> <tr> <th>R¹</th><th>R²</th><th>R³</th><th>R⁴</th></tr> <tr> <td>MeO</td><td>H</td><td>—OCH₂O—</td><td>(63)</td></tr> <tr> <td>H</td><td>MeO</td><td>H</td><td>MeO (80)</td></tr> <tr> <td>H</td><td>MeO</td><td>MeO</td><td>MeO (54)</td></tr> <tr> <td>MeO</td><td>H</td><td>MeO</td><td>MeO (85)</td></tr> </table>	R ¹	R ²	R ³	R ⁴	MeO	H	—OCH ₂ O—	(63)	H	MeO	H	MeO (80)	H	MeO	MeO	MeO (54)	MeO	H	MeO	MeO (85)	305
R ¹	R ²	R ³	R ⁴																					
MeO	H	—OCH ₂ O—	(63)																					
H	MeO	H	MeO (80)																					
H	MeO	MeO	MeO (54)																					
MeO	H	MeO	MeO (85)																					

C₁₇₋₁₈

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
<div> <p>C₁₇₋₁₉</p> </div>	Et ₃ SiH (3 eq), TiCl ₄ , CH ₂ Cl ₂ , 0°	<div> <p>305</p> </div>	
<div> <p>C₁₈</p> </div>	Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 45 min Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 90 min Et ₃ SiH (4.0 eq), (C ₆ F ₅) ₃ P (5 mol%), CH ₂ Cl ₂ , rt, 20 h	<div> <p>(100) + Me₃CH (—)</p> </div> <div> <p>(100) + Me₃CH (—)</p> </div> <div> <p>(96)</p> </div>	307 307 282

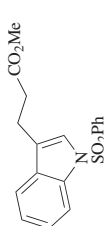
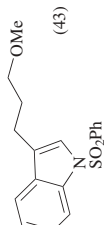
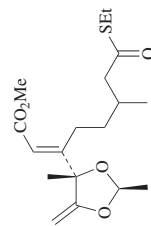
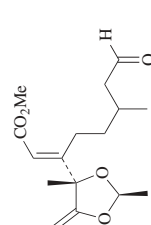
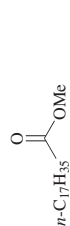

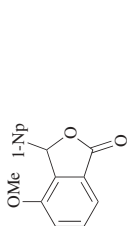
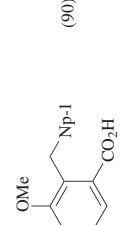

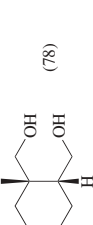
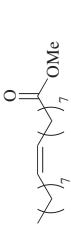



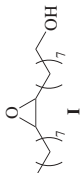


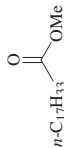


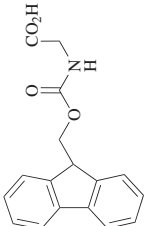
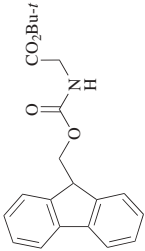
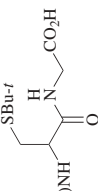
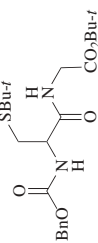
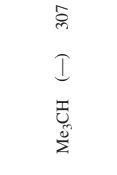
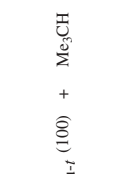
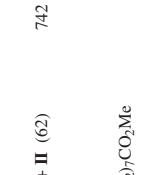
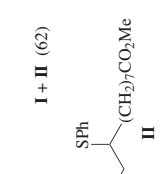

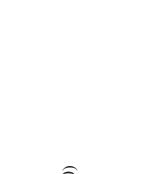


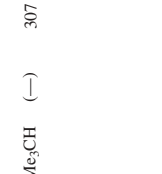
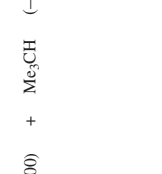
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		Et ₃ SiH (2-3 eq), Pd/C (2-5 mol%), acetone, rt, 30-60 min	300
		Et ₃ SiH (6 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 20 h	281
		1. EtMe ₂ SiH (4 eq), 223 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add ester, 6 h	280
		Et ₃ SiH (xs), TFA	304
		PMHS (10 eq), Ti(OPr- <i>i</i>) ₄ (1 eq), THF	279
		PMHS (2.5 eq), Ti(OPr- <i>i</i>) ₄ (100 mol%), 65°, 24 h	292
		PMHS (2.5 eq), Cp ₂ TiCl ₂ (2 mol%), <i>n</i> -BuLi (2 eq), THF, rt, 1.5 h	289

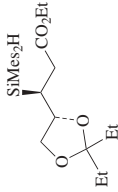
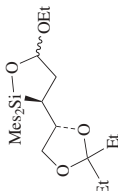
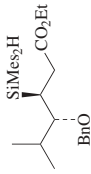
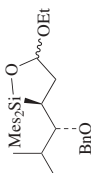
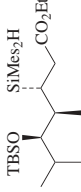
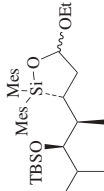
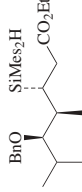
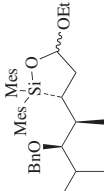
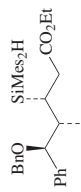
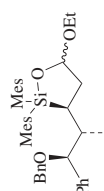
TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ref.	Product(s) and Yield(s) (%)	Conditions	Ester	Ref.
C ₁₉	 (92)	(EtO) ₃ SiH (2.5-3.0 eq), Ti(OPr- <i>i</i>) ₄ (5 mol%), 40 to 55°, 10h		291
	 I (85)	PMHS (2.5 eq), Ti(OPr- <i>i</i>) ₄ (100 mol%), 65°, 5 h		292
	 (32) + <i>n</i> -C ₁₇ H ₃₃ CH ₂ OMe (22)	PMHS (2.5 eq), (EBTHD)TiCl ₂ (5 mol%), <i>n</i> -BuLi (2 eq), THF, rt, 1 h 1. EtMe ₂ SiH (4 eq), 223 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add ester, 6 h		289
C ₂₀	 (90)	1. (EBTHD) ₂ TiCl ₂ (5 mol%), <i>n</i> -BuLi (10 mol%), THF, -15°, 15 min 2. (EtO) ₃ SiH (2 eq), ester addition, -20° to rt, 8 h		290
C ₂₁	 (85) + Me ₃ CH (—)	Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 20 min		307
	 (78) + Me ₃ CH (—)	Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 40 min		307

C ₂₁		(EtO) ₃ SiH (1.1 eq), CsF (1 eq), 60°, 9 h		(75)	79
C ₂₂		Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 30 min		(98) + Me ₃ CH (—)	307
C ₂₅		PMHS (5 eq), Cp ₂ Ti(OC ₆ H ₄ Cl-4) ₂ (5 mol%), TBAF/alumina (1 mol%), MeC ₆ H ₅ , rt		(92)	302
C ₂₆		1. Et ₃ SiH (5 eq), Pd/C (15 mol%), CH ₂ Cl ₂ , rt, 40 min 2. Camphorsulfonic acid (0.1 eq), MeOH 3. TBAF, AcOH, MeOH		(65)	300
		Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 35 min		(83) + Me ₃ CH (—)	307

TABLE 10. ORGANOSILANE REDUCTION OF ESTERS AND LACTONES (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₇	 BOCNH-CH(Ph)-CH2-C(=O)-NH-CH2-C(=O)-O-C(=O)-Bu-t Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 75 min	 H ₂ N-CH(Ph)-CH2-C(=O)-NH-CH2-C(=O)-O-C(=O)-Bu-t + Me ₃ CH (—)	307
C ₂₈	 n-C ₈ H ₁₇ -CH(SPh)-CH(OAc)-CH2-C(=O)-O-C(=O)-Me + n-C ₈ H ₁₇ -CH(SPh)-CH2-C(=O)-O-C(=O)-Me BnMe ₂ SiH, TFA, rt, 20 h	 I + II (62)	742
C ₂₈	 n-C ₈ H ₁₇ -CH(SPh)-CH2-C(=O)-O-C(=O)-Me (EtO) ₃ SiH, CsF, rt, 72 h	 (80)	83
C ₂₈	 n-C ₈ H ₁₇ -CH(SPh)-CH2-C(=O)-O-C(=O)-Me Et ₃ SiH (1.5 eq), BF ₃ •OEt ₂ (1.1 eq), -20°, 24 h	 (65)	510
C ₂₈	 n-C ₈ H ₁₇ -CH(SPh)-CH2-C(=O)-O-C(=O)-Me Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 95 min	 (100) + Me ₃ CH (—)	307

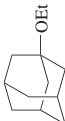







C ₂₉		TBAF (10 mol%), 0°		(91) dr = 98:2	743
C ₃₃		TBAF (10 mol%), 0°		(-) dr = 96:4	743
C ₃₅		TBAF (10 mol%), 0°		(-) dr = 96:4	743
C ₃₆		TBAF (10 mol%), 0°		(82) dr = 85:15	743
C ₃₉		TBAF (10 mol%), 0°		(79) dr = 93:7	743

^a The yield was determined by NMR spectroscopy.

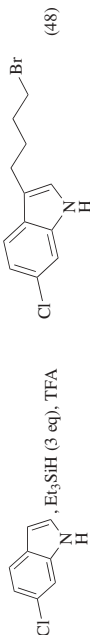
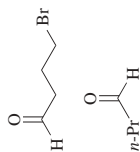
^b No reduction occurred in this reaction.

^c The product was isolated as the phenylhydrazone.

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.													
C ₂ 	Me ₃ SiH (1.25 eq), TMSI (0.3 eq), 1-AdOTMS (1.25 eq), <i>n</i> -C ₅ H ₁₂ , −78° to rt, 5–6 h	(69)	338													
C ₂₋₇ 	Et ₃ SiH (3 eq), TFA (2.9 eq), PhCONH ₂ , solvent, 18 h	<table><tr><th>R</th><th>Solvent</th><th>Temp</th></tr><tr><td>Me</td><td>MeCN</td><td>22°</td></tr><tr><td><i>i</i>-Bu</td><td>MeC₆H₅</td><td>120°</td></tr><tr><td><i>c</i>-C₆H₁₁</td><td>MeC₆H₅</td><td>120°</td></tr></table>	R	Solvent	Temp	Me	MeCN	22°	<i>i</i> -Bu	MeC ₆ H ₅	120°	<i>c</i> -C ₆ H ₁₁	MeC ₆ H ₅	120°	(95) (90) (92)	326
R	Solvent	Temp														
Me	MeCN	22°														
<i>i</i> -Bu	MeC ₆ H ₅	120°														
<i>c</i> -C ₆ H ₁₁	MeC ₆ H ₅	120°														
C ₂₋₇ 	Et ₃ SiH, HClO ₄ , MeCN, rt		(—)	380												
C ₃ 	Et ₃ SiH (2 eq), TMSOTf (0.1 eq), CH ₂ Cl ₂ , rt, 2 h Et ₃ SiH, TMSOTf, <i>c</i> -C ₆ H ₁₁ OTMS ₃ , CH ₂ Cl ₂ , 0°, 2 h		(100) ^a (100) ^a	334 334												
C ₄₋₇ 	Ph(Np-1) ₂ SiH ₂ , CIRh(PPh ₃) ₃ (5x10 ^{−4} M) R = <i>n</i> -Pr, Ph		(—)	744												

R = Me, Et, *i*-Pr, *n*-Bu, Ph,
4- ClC_6H_4 , 4- MeC_6H_4 , 4- NCC_6H_4

C₄

355

See table.



Conditions	Temp	Time	R	
Et ₃ SiH, TMSOTf, <i>c</i> -C ₆ H ₁₁ OTMS, CH ₂ Cl ₂	0°	2 h	<i>c</i> -C ₆ H ₁₁	(100) ^a
Et ₃ SiH, TFA	30-40°	—	CH ₂ Pr- <i>n</i>	(37)
Et ₃ SiH, TFA, EtOH	50-60°	8 h	Et	(78)
TMSH, TMSI, <i>c</i> -C ₆ H ₁₁ OTMS, CH ₂ Cl ₂	0°	2 h	<i>c</i> -C ₆ H ₁₁	(100)
Et ₃ SiH, TMSI, <i>n</i> -C ₈ H ₁₇ OTMS, CH ₂ Cl ₂	0°	2 h	<i>n</i> -C ₈ H ₁₇	(100)

334

311

327

334

334

C₄₋₉

Et₃SiH (1.2 eq), R²OTMS (1.2 eq),
 BiBr₃ (10-30 mol%), rt



343

303

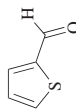
R ²	Time	
Bn	2 h	(76)
Bn	<5 min	(58)
Bn	<5 min	(84)
Ph	1 h	(0)
2-octyl	1 h	(81)
Bn	<5 min	(86)
Bn	1 h	(83)

C₄₋₇

Et₃SiH (1 eq), EtOH (x eq),
 TFA (y eq), 50-60°

R	x	y	
<i>n</i> -C ₃ H ₇	2	4	(78)
<i>n</i> -C ₄ H ₉	2	4	(57)
Ph	3	5	(89)

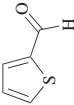

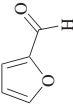
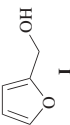



327

C₅

Et₃SiH (4 eq), TFA (8 eq),
 50°, 30 h

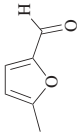


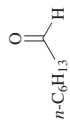

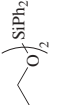

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TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅ 	PhMe ₂ SiH (1.1 eq), CsF (10 mol%), 18-C-6 (5 mol%), CH ₂ Cl ₂ , rt, 3 h	 (54)	346, 347
	(EtO) ₃ SiH (1.1 eq), KF (1 eq), rt, 1 h	 (85)	79
	Me(EtO) ₂ SiH (1.1 eq), KF (1 eq), rt, 18 h	I (90)	79
	H , 0°, 2 h	<i>t</i> -Bu-CH ₂ -OH (92)	93
	Et ₃ SiH (1 eq), HC(OEt) ₃ (1 eq), EtOH, HCl, TFA (3 eq), 50-60°, 6-8 h	<i>n</i> -Bu-CH ₂ -O-Et (72)	327
	Et ₃ SiH, TFA, 30-40°	<i>n</i> -Bu-CH ₂ -O-CH ₂ -Bu- <i>n</i> (50)	311
	(HMe ₂ Si) ₂ O, TMSOTf, C ₆ H ₆ , 80°, 30 min	I (90)	314
	(HMe ₂ Si) ₂ O, TMSCl, NaI, MeCN, rt, 30 min	I (84)	314, 356
	(HMe ₂ Si) ₂ O, TFA, EtOH, 50-60°, 8 h	I (57)	327
	(HMe ₂ Si) ₂ O, TFA, HCl, EtOH, HC(OEt) ₃ , 50-60°, 8 h	I (72)	329
	Et ₃ SiH, ZnCl ₂	R-CH ₂ -O-CH ₂ -R (52)	330
	R = <i>i</i> -Bu, <i>s</i> -Bu		

C ₅₋₉	$\text{Ar}-\text{C}(=\text{O})-\text{H}$	$\text{R}-\text{C}(\text{OSiMe}_2\text{H})=\text{CH}-\text{CH}(\text{OSiMe}_2\text{H})-\text{Ar}$	$\text{R}-\text{C}(\text{OH})=\text{CH}-\text{CH}(\text{OH})-\text{Ar}$	$\text{I} + \text{II} \rightarrow \text{II}$	400
	Ar	R	Z:E	$\text{I} + \text{II}$	
	2-C ₄ H ₉ O	Ph	>98:2	(73)	91:9
	Ph	Et	74:26	(64)	68:32
	Ph	<i>i</i> -Pr	75:25	(64)	88:12
	Ph	<i>t</i> -Bu	>98:2	(65)	99:1
	4-O ₂ NC ₆ H ₄	Ph	>98:2	(84)	85:15
	4-MeC ₆ H ₄	Ph	>98:2	(87)	96:4
	4-MeOC ₆ H ₄	Ph	>98:2	(74)	94:6
	BnCH ₂	Ph	>98:2	(43)	82:18
C ₅₋₁₁	$\text{R}-\text{C}(=\text{O})-\text{H}$	$\text{R}-\text{CH}_2-\text{OH}$	Cl_3SiH (1.5 eq), CH ₂ Cl ₂ /DMF (4:1), 0°, 4-6 h	R	318
				2-C ₄ H ₉ O	(81)
				2-C ₄ H ₉ S	(99)
				Ph	(98)
				4-ClC ₆ H ₄	(95)
				4-O ₂ NC ₆ H ₄	(98)
				4-MeOC ₆ H ₄	(100)
				BnCH ₂	(98)
				(<i>E</i>)-PhCH=CH	(87)
				PhC≡C	(72)
				H ₂ C=CH(CH ₂) ₈	(80)
C ₅	$\text{C}_5-\text{C}(=\text{O})-\text{H}$	$\text{C}_5-\text{C}(\text{OSiMe}_2\text{H})=\text{CH}-\text{CH}(\text{OSiMe}_2\text{H})-\text{C}_5$	PhMe_2SiH (1.1 eq), CsF (0.1 eq), 18-C-6 (0.05 eq), CH ₂ Cl ₂ , rt, 11 h	C_5	347
C ₆	$\text{C}_6-\text{C}(=\text{O})-\text{H}$	$\text{C}_6-\text{C}(\text{OSiMe}_2\text{H})=\text{CH}-\text{CH}(\text{OSiMe}_2\text{H})-\text{C}_6$	Ph_2SiH_2 (1.1 eq), TBAF (5 eq), HMPA, rt, 2.5 h	C_6	320

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	PhMe ₂ SiH (1.1 eq), CsF (10 mol%), 18-C-6 (5 mol%), CH ₂ Cl ₂ , rt, 0.5 h	 (58)	346, 347
	PhMe ₂ SiH (1.1 eq), CsF (10 mol%), 18-C-6 (0.5 mol%), CH ₂ Cl ₂ , rt	Ar-CH=CH-OSiMe ₂ Ph	345
C ₇ 	<div>Ar</div> <div>Time</div> <div>2-pyridinyl</div> <div>3-pyridinyl</div> <div>4-pyridinyl</div>	<div>(67)</div> <div>(54)</div> <div>(60)</div>	
	Ph ₂ SiH ₂ (0.5 eq), 1,2-C ₆ H ₄ (CO ₂ K) ₂ , 100°, 24 h	 I (60)	319
	Ph ₂ SiH ₂ (0.5 eq), KF, 100°, 6 h	I (50)	319
	Ph ₂ SiH ₂ (0.5 eq), CsF, rt, 3 min	 (100)	83, 319
	(EtO) ₃ SiH (1.1 eq), KF (1 eq), rt, 4 h	 II (70)	79, 83
	Et ₃ SiH (1.1 eq), HCl, 28°, 3 h	II (100)	313
	Et ₃ SiH (1.25 eq), H ₂ SO ₄ , H ₂ O (11 eq), 28°, 1.25 h	II (97)	313
	Me(EtO) ₂ SiH (1.5 eq), KF (1 eq), DMF, 10°, 1.75 h	I (85)	83
	1. Cyclohexanone, Me(EtO) ₂ SiH (1.2 eq), KO ^t CH (1 eq), DMF, 45°, 19 h 2. H ₃ O ⁺	II (72) + <i>n</i> -C ₆ H ₁₀ O (recovered)	82

HMe ₂ SiOSiMe ₂ H (1.0 eq), TMSOTf (cat.), C ₆ H ₆ , 80°, 30 min	<i>n</i> -C ₆ H ₁₃ —O—C ₆ H ₁₃ - <i>n</i> (96)	314
Et ₃ SiH, TFA, rt, 45 min	III (90)	313
PhMe ₂ SiH, EG acid, CH ₂ Cl ₂ , rt,	III (92)	333
Et ₃ SiH, ZnCl ₂	III (48)	330
(HMe ₂ Si) ₂ O, TMSCl, C ₆ H ₆ , rt, 30 min	III (96)	330
(HMe ₂ Si) ₂ O, TMSCl, NaI, C ₆ H ₆ , rt, 30 min	III (90)	314
Et ₃ SiH, H ₂ SO ₄ , MeOH, rt, 1 h	III (87)	328
TMSh, TMSI, TMSOEt, CH ₂ Cl ₂ , 0°, 2 h	III (90)	334
Et ₃ SiH, TFA, BnOH, rt, 1 h	<i>n</i> -C ₆ H ₁₃ —OBn (49)	328
PhMe ₂ SiH, EG acid	<i>n</i> -C ₆ H ₁₃ —O—CH ₂ CH ₂ Ph (82)	333
TMSh (1.1 eq), TMSI (5 mol%), EtOTMS (1 eq), CH ₂ Cl ₂ , 0-15°, rt, 2 h	<i>n</i> -C ₆ H ₁₃ —OEt (90)	334
(EtO) ₃ SiH (2.3 eq), KF (1 eq), rt, 20 h	CH ₃ (CH ₂) ₆ OH (100) + PhC(=O)Ph (0)	83
TMSh (1.25 eq), TMSI (0.3 eq), <i>n</i> -C ₃ H ₁₂ , -78° to rt, 5-6 h, <i>t</i> -BuOTMS (1.25 eq)	<i>n</i> -C ₆ H ₁₃ —OBu- <i>t</i> (63)	338

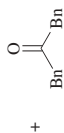


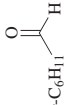

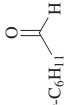


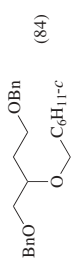
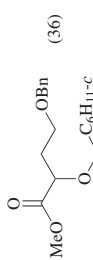
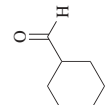
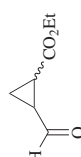
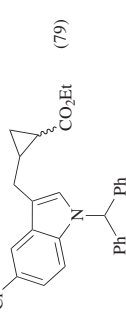


TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)


Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.									
	1. $SnCl_4$, $TMSCl$, SnI_2 , CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h	 (89)	306									
	1. $Ti-SnCl_6$ (5–30 mol%), CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h	 I (91)	306									
	$PhSiH_3$ (0.4 eq), $Mn(dpm)_3$ (3 mol%), i -PrOH, DCE, O_2 , rt 2. Et_3SiH (1.5 eq), -23° , 2.5 h	 (92)	367									
	t -BuOTMS (1.25 eq), $TMSH$ (1.25 eq), $TMSI$ (0.3 eq), n - C_8H_{17} , -78° to rt, 5–6 h	 (84)	338									
	$BnOCH_2CH_2CH_2OTMS$, Et_3SiH (1 eq), $TMSOTf$ (0.1 eq), CH_2Cl_2 , -30°	 (84)	341									
	$MeO-C(=O)-CH_2CH_2OTMS$, Et_3SiH (1 eq), $TMSOTf$ (0.1 eq), CH_2Cl_2 , -30°	 (36)	341									
	R_3SiH (x eq), $(Ph_3P)CuH$ (3 mol%), MeC_6H_5	<table><tr><th>R_3Si</th><th>x</th><th>Time</th></tr><tr><td>$PhMe_2Si$</td><td>1.3</td><td>2 h (95)</td></tr><tr><td>Ph_2MeSi</td><td>2.5</td><td>— (98)</td></tr></table>	R_3Si	x	Time	$PhMe_2Si$	1.3	2 h (95)	Ph_2MeSi	2.5	— (98)	317
R_3Si	x	Time										
$PhMe_2Si$	1.3	2 h (95)										
Ph_2MeSi	2.5	— (98)										
	5-Chloro- N -benzhydrylindole, Et_3SiH (3 eq), TFA	 (79)	355									



Et ₃ SiH (1.1 eq), Fe-mont, rt, 0.3 h	 I (80)	353
(EtO) ₃ SiH (1.1 eq), HAp, rt, 0.3 h	I (72)	353
(EtO) ₃ SiH (1.1 eq), CaO, rt, 0.3 h	I (59)	353
Et ₃ SiH (1 eq), (Ph ₃ P) ₃ RhCl (0.1 mol%), rt, 5 min	 (95)	411
PMHS (10% xs), [Bu ₂ (AcO)Sn] ₂ O (2 mol%), EtOH, reflux	 II (100)	316
PMHS, Pd/C, EtOH, 80°	PhMe (84)	316
PMHS, TMSOTf (cat.), C ₆ H ₆ , reflux, 2 h	 (92)	314
PMHS, TMSOTf (cat.), MeC ₆ H ₅ , reflux, 1 h	 III + IV (95)	314
(EtO) ₃ SiH (2.3 eq), KF (1 eq), rt, 6 h	II (90)	83
Me(EtO) ₂ SiH (2.3 eq), KF (1 eq), DMF, 20°, 0.25 h	II (90)	83
Me(EtO) ₂ SiH, KF, 20°, 0.25 h	II (90)	83
Silane, salt, solvent	II	82

Silane	Salt	Solvent	Temp	Time
Me(EtO) ₂ SiH	KF	DMF	20°	0.25 h (90)
PMHS	KF•2H ₂ O	DMF	35°	1 h (76)
PMHS	KF•2H ₂ O	DMSO	rt	1 h (67)
PMHS	KO ₂ CH	DMF	80°	4 h (64)
Me(EtO) ₂ SiH	KO ₂ CH	DMF	80°	11 h (75)

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	<p>PMHS (1 eq), ZnCl_2 (1 eq), Et_2O, rt, 24 h</p> <p>Et_3SiH, TBAF, MeCN, 12 h</p> <p>Et_3SiH, CsF, MeCN, 12 h</p> <p>G, 0°, 2 h</p> <p>PhSiH_3 (0.4 eq), $\text{Mn}(\text{dpm})_3$ (3 mol%), <i>i</i>-PrOH, DCE, O_2, rt</p> <p>K, CH_2Cl_2, rt, 2 h</p> <p>J, THF, 0°, 2 h</p> <p>L, THF, 0°, 2 h</p> <p>M, LiCl (4 eq), THF, 0°, 2 h</p> <p>Et_3SiH (1.1 eq), $\text{BF}_3\cdot\text{OEt}_2$ (2.0 eq), rt</p> <p>Et_3SiH, TFA, $30\text{--}40^\circ$</p> <p>$\text{Et}_3\text{SiO}(\text{EtHSiO})_n\text{SiEt}_3$ (0.5 mol%), TFA (8 eq), CHCl_3, 50°, 1 h</p> <p>Et_3SiH (2 eq), TMSOTf (0.1 eq), CH_2Cl_2, rt, 2 h</p>	<p>Ph-CH₂-OH (72) II</p> <p>II (36)</p> <p>II (96)</p> <p>II (96)</p> <p>II (68)</p> <p>II (95)</p> <p>II (95)</p> <p>II (61)</p> <p>II (69)</p> <p>I (75) + II (25)</p> <p>I (80)</p> <p>I (92)</p> <p>I (major) + II (minor)</p>	<p>315</p> <p>77</p> <p>77</p> <p>93</p> <p>367</p> <p>101</p> <p>96</p> <p>96</p> <p>96</p> <p>74</p> <p>311</p> <p>207</p> <p>334</p>

(HM ₂ Si) ₂ O, TFA, EtOH, 30-40°	I (80)	313
Et ₃ SiH, TFA, rt, 30 min	I (87)	313
Et ₃ SiH, TFA, CHCl ₃ , rt, 15 min	I (93)	313
Et ₃ SiH, TFA, CCl ₄ , rt, 15 min	I (89)	313
Et ₃ SiH, TFA, MeCN, rt, 15 min	I (96)	313
Et ₃ SiH, Cl ₂ CHCO ₂ H, rt, 30 min	I (93)	313
Et ₃ SiH, BF ₃ •OEt ₂ , rt, 1 h	I (75)	333
Et ₃ SiH, EG acid, CH ₂ Cl ₂ , rt	I (91)	333
PhMe ₂ SiH, EG acid, CH ₂ Cl ₂ , rt	I (96)	74
Et ₃ SiH, TlClO ₄ , CH ₂ Cl ₂ , 0°, 10 min	I (84)	329
Et ₃ SiH, TlClO ₄ , BnOTMS, CH ₂ Cl ₂ , 0°, 10 min	I (72)	329
(HM ₂ Si) ₂ O, TMSOTf, C ₆ H ₆ , 80°, 20 min	I (97)	314
Cl ₃ SiH (3 eq), (<i>n</i> -Pr) ₃ N (1 eq), MeCN, 57-58°, 1 h	Ph-CH ₂ -SiCl ₃ (5) +  (42)	711

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 $\text{Ph}-\text{C}(=\text{O})-\text{H}$	Et_3SiH (1.4 eq), TBAF (1.4 eq), MeCN, rt, 12 h	$\text{Ph}-\text{CH}(\text{OSiEt}_3)-\text{H}$ V (96) (36)	76
	Et_3SiH (1.5 eq), CsF (1.5 eq), MeCN, rt, 10 h	V (96)	76
	PhMe_2SiH (1.2 eq), TBAF (2 eq), HMPA, rt, 1.5 h	$\text{Ph}-\text{CH}(\text{OSiMe}_2\text{Ph})-\text{H}$ VI (91)	320
	PhMe_2SiH (1.1 eq), CsF (0.1 eq), 18-C-6 (0.05 eq), CH_2Cl_2 , rt, 11 h	VI (57)	347
	R_3SiH (1.5 eq), catalyst, MeC_6H_5	OSiR_3 $\text{Ph}-\text{CH}(\text{H})-\text{H}$	324
	R_3Si	Catalyst	Temp
	Et_3Si	Fe-mont	rt
	PhMe_2Si	Fe-mont	rt
	$(\text{EtO})_3\text{Si}$	Fe-mont	40°
	Et_3Si	Cu-mont	rt
	Et_3Si	Na-mont	rt
	Et_3Si	silica	rt
	Et_3Si	Ca-Y-zeolite	rt
	Et_3SiH (1.1 eq), ROH, acid, 28°	$\text{Ph}-\text{CH}(\text{OR})-\text{H}$	328
R	Acid		
	Me	H_2SO_4	(87)
	Me	$\text{CF}_3\text{-CO}_2\text{H}$	(87)
	Me	$\text{CCl}_3\text{CO}_2\text{H}$	(85)
	Et	H_2SO_4	(87)
	<i>n</i> -Pr	H_2SO_4	(68)
	<i>i</i> -Pr	H_2SO_4	(69)
	<i>n</i> -C ₇ H ₁₅	$\text{CF}_3\text{CO}_2\text{H}$	(81)
	<i>t</i> -Bu	$\text{CF}_3\text{CO}_2\text{H}$	(26)
	<i>t</i> -Bu	H_2SO_4	(45)


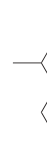



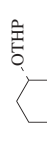
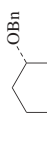

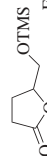
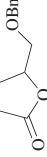
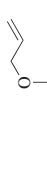

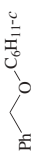

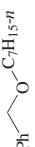
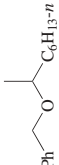







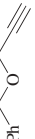
 $\text{Ph}-\text{CH}_2-\text{CH}(\text{Me})-\text{CH}_2-\text{OTHP}$, Et_3SiH (2.2 eq), TMSOTf (10 mol%), MeCN , 0° , 1 h	 $\text{Ph}-\text{CH}_2-\text{CH}(\text{Me})-\text{CH}_2-\text{OBn}$ (95)	340
$\text{BnO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OTHP}$, Et_3SiH (2.2 eq), TMSOTf (10 mol%), MeCN , 0° , 1 h	 $\text{BnO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OBn}$ (95)	340
$\text{AcO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OTHP}$, Et_3SiH (2.2 eq), TMSOTf (10 mol%), MeCN , 0° , 1 h	 $\text{AcO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OBn}$ (98)	340
$\text{Ar}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OTHP}$, Et_3SiH (2.2 eq), TMSOTf (10 mol%), MeCN , 0° , 1 h	 $\text{Ar}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OBn}$ (98) $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$	340
 $\text{Ph}-\text{C}_6\text{H}_{11}-\text{OTHP}$, Et_3SiH (2.2 eq), TMSOTf (10 mol%), MeCN , 0° , 1 h	 $\text{Ph}-\text{C}_6\text{H}_{11}-\text{OBn}$ (97)	340
1-AdOTMS (1.25 eq), TMSH (1.25 eq), TMSI (0.3 eq), $n\text{-C}_5\text{H}_{12}$, -78° to rt, 5-6 h	 $1\text{-Ad}-\text{OBn}$ (75)	338
 OTMS , Et_3SiH (1 eq), TMSOTf (0.1 eq), CH_2Cl_2 , 0° to rt	 OBn (89)	341
 $\text{AcO}-\text{BnO}$, OTMS , Et_3SiH (1 eq), TMSOTf (2.0 eq), CH_2Cl_2 , -78° to -30°	 $\text{AcO}-\text{BnO}$ (96)	341
TMSH , TMSI , $c\text{-C}_6\text{H}_{11}\text{OTMS}$, CH_2Cl_2 , 0° , 2 h	 $\text{Ph}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OBn}$ (98)	334

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	Et_3SiH , TFA, $n-C_7H_{15}OH$, rt, 1 h	 (81)	328
	Et_3SiH , Ph_3CClO_4 , $n-C_6H_{13}CH(Me)OTMS$, CH_2Cl_2 , 0° , 10 min	 (—)	329
	$PhMe_2SiH$, EG acid, $Ph(CH_2)_3OTMS$, CH_2Cl_2 , rt,	 (99)	333
	Et_3SiH , Ph_3CClO_4 , $Ph(CH_2)_3OTMS$, CH_2Cl_2 , 0° , 10 min	 (83)	329
	$PhMe_2SiH$, EG acid, $TMSO(CH_2)_2OTMS$, CH_2Cl_2 , rt,	 (63)	333
	 catalyst (10 mol%), $MeCN$, 0° , 1 h	 (87)	340
	Catalyst		
	$Sn(OTf)_2$	(96)	
	$BF_3 \cdot OEt_2$	(20)	
	TMSI	(88)	
	TMSOTf	(98)	
	Et_3SiH , TFA, $MeOH$, rt, 1 h	 (87) VII	328
	Et_3SiH , Cl_3CCO_2H , $MeOH$, rt, 1 h	VII (85)	328
	Et_3SiH , H_2SO_4 , $EtOH$, rt, 1 h	 (87)	328
	Et_3SiH , EG acid, $TMSOCH_2C \equiv CH$, CH_2Cl_2 , rt,	 (95)	333

Et ₃ SiH, EG acid, TMSOCH ₂ CH=CH ₂ , CH ₂ Cl ₂ , rt,	Ph-CH ₂ -O-CH=CH ₂ (71)	333
Et ₃ SiH, H ₂ SO ₄ , <i>n</i> -PrOH, rt, 1 h	Ph-CH ₂ -O-Pr- <i>n</i> (68)	328
Et ₃ SiH, H ₂ SO ₄ , <i>i</i> -PrOH, rt, 1 h	Ph-CH ₂ -O-Pr- <i>i</i> (69)	328
Et ₃ SiH, H ₂ SO ₄ , <i>t</i> -BuOH, rt, 1 h	Ph-CH ₂ -O-Bu- <i>t</i> (45)	328
1. HC(OMe) ₃ , CH ₂ Cl ₂ , rt, 2 h 2. Et ₃ SiH, Nafion [®] -H, CH ₂ Cl ₂ , reflux, 3 h	VII (94,6)	335
Et ₃ SiH (1 eq), MeOH (2 eq), TFA (4 eq), 50 to 60°	VII (83)	327
Et ₃ SiH (1 eq), TMSOTf (0.1 eq), ROTMS (0.83 eq), CH ₂ Cl ₂	Ph-CH ₂ -O-R	341
	R	Temp
	Bn	-78° to -30° (96)
	H ₂ C=CHCH ₂	-30° to 0° (99)
	<i>i</i> -Bu	0° to rt (81)
	<i>i</i> -Pr	0° to rt (92)
	<i>c</i> -C ₆ H ₁₁	-78° to -30° (99)
	<i>t</i> -Bu	0° to rt (16)
	Ph	0° to rt (0)



(EtO)₃SiH (2.3 eq), KF (1 eq), rt, 36 h II (100) 83

PDMS (2.3 eq), K₂CO₃ (1 eq), 60°, 2.5 h II (100) 83

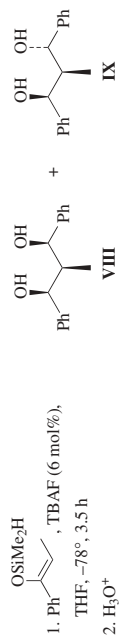




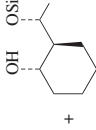
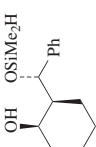
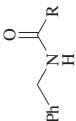

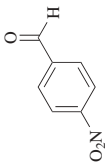
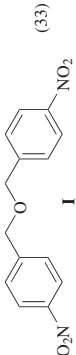
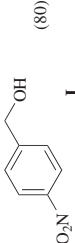
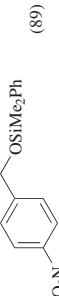
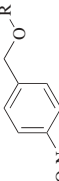


TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.																																																												
<div>C-7</div> <div></div>	<div></div> , TBAF (6 mol%), -78°, 15 h	<div></div> X + <div></div> XI	400																																																												
		<div></div> XII + <div></div> XIII																																																													
	X + XI + XII + XIII (75), X.XI:XII:XIII = 27:6:53:14																																																														
	Et ₃ SiH (3 eq), TFA (2-3 eq), RCONH ₂ , PhCHO (x eq), solvent	<div></div>	326																																																												
	<table><tr><th>R</th><th>Solvent</th><th>Temp</th><th>Time</th><th>x = 0.33</th><th>x = 3</th></tr><tr><td>Bn</td><td>MeC₆H₅</td><td>120°</td><td>36 h</td><td>(92)</td><td>(68)</td></tr><tr><td>Ph</td><td>MeC₆H₅</td><td>120°</td><td>18 h</td><td>(91)</td><td>(94)</td></tr><tr><td>4-FC₆H₄</td><td>MeC₆H₅</td><td>120°</td><td>18 h</td><td>(92)</td><td>(93)</td></tr><tr><td>4-MeOC₆H₄</td><td>MeC₆H₅</td><td>120°</td><td>18 h</td><td>(95)</td><td>(91)</td></tr><tr><td>PhO</td><td>MeCN</td><td>22°</td><td>18 h</td><td>(90)</td><td>(85)</td></tr><tr><td>BnO</td><td>MeCN</td><td>22°</td><td>18 h</td><td>(95)</td><td>(92)</td></tr><tr><td><i>t</i>-BuO</td><td>MeCN</td><td>22°</td><td>18 h</td><td>(92)</td><td>(81)</td></tr><tr><td>PhNH</td><td>MeC₆H₅</td><td>22°</td><td>18 h</td><td>(92)</td><td>(97)</td></tr><tr><td>BnNH</td><td>MeC₆H₅</td><td>22°</td><td>18 h</td><td>(89)</td><td>(88)</td></tr></table>	R	Solvent	Temp	Time	x = 0.33	x = 3	Bn	MeC ₆ H ₅	120°	36 h	(92)	(68)	Ph	MeC ₆ H ₅	120°	18 h	(91)	(94)	4-FC ₆ H ₄	MeC ₆ H ₅	120°	18 h	(92)	(93)	4-MeOC ₆ H ₄	MeC ₆ H ₅	120°	18 h	(95)	(91)	PhO	MeCN	22°	18 h	(90)	(85)	BnO	MeCN	22°	18 h	(95)	(92)	<i>t</i> -BuO	MeCN	22°	18 h	(92)	(81)	PhNH	MeC ₆ H ₅	22°	18 h	(92)	(97)	BnNH	MeC ₆ H ₅	22°	18 h	(89)	(88)		
R	Solvent	Temp	Time	x = 0.33	x = 3																																																										
Bn	MeC ₆ H ₅	120°	36 h	(92)	(68)																																																										
Ph	MeC ₆ H ₅	120°	18 h	(91)	(94)																																																										
4-FC ₆ H ₄	MeC ₆ H ₅	120°	18 h	(92)	(93)																																																										
4-MeOC ₆ H ₄	MeC ₆ H ₅	120°	18 h	(95)	(91)																																																										
PhO	MeCN	22°	18 h	(90)	(85)																																																										
BnO	MeCN	22°	18 h	(95)	(92)																																																										
<i>t</i> -BuO	MeCN	22°	18 h	(92)	(81)																																																										
PhNH	MeC ₆ H ₅	22°	18 h	(92)	(97)																																																										
BnNH	MeC ₆ H ₅	22°	18 h	(89)	(88)																																																										
	Me ₂ ClSiH (1.2 eq), In(OH) ₃ (5 mol%), CHCl ₃ , rt, 5.5 h	<div></div> XIV	331																																																												
	Me ₂ ClSiH (1.2 eq), InCl ₃ (5 mol%), CHCl ₃ , rt, 5.5 h	XIV (60)	331																																																												

	1. R ² SH, BF ₃ •OEt ₂ , CH ₂ Cl ₂ , 0°, 1 min 2. Et ₃ SiH, 0° to rt, 3 h		R ¹ R ² Ph Ph (91) Ph <i>i</i> -Pr (97) Ph <i>n</i> -Bu (94) Ph <i>s</i> -Bu (92) <i>n</i> -C ₆ H ₁₃ <i>i</i> -Pr (86) (74) 95% ee	365
	MesPhSiH ₂ , [Rh(cod)Cl] ₂ (2.5 mol%), (-)- 4 , THF, rt			586
	PMHS, TMSOTf (cat.), C ₆ H ₆ , reflux, 3 h		Ar Ar I II 2-ClC ₆ H ₄ (25) I + II (65) 4-ClC ₆ H ₄ I : II = 75:25	314
	Et ₃ SiH, TFA, 0°, 10 h	II Ar = 4-ClC ₆ H ₅ (80)		313
	PhMe ₂ SiH, EG acid, CH ₂ Cl ₂ , rt,	II Ar = 4-ClC ₆ H ₅ (86)		333
	(HMe ₂ Si) ₂ O, TMSOTf, C ₆ H ₆ , 80°, 20 min	II Ar = 4-ClC ₆ H ₅ (90)		314
	Et ₃ SiH (1.2 eq), TMSCl (1.2 eq), In(OH) ₃ (5 mol %), CHCl ₃ , rt, 2 h		I	331
	Me ₂ ClSiH (1.2 eq), In(OH) ₃ (5 mol%), CHCl ₃ , rt, 2 h	I (34)		331
	Cl ₃ SiH (3 eq), (<i>n</i> -Pr) ₃ N (1 eq), MeCN, 51-64°, 1 h		(61)	711
	(EtO) ₃ SiH (1.1 eq), KF (1 eq), 100°, 1 h		(90)	79, 80

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.						
									
C ₇									
	Et ₃ SiH, TFA, rt, 5 h	 I (55) (33)	313						
	(HMec ₂ Si) ₂ O, TMSOTf, CH ₂ Cl ₂ , 30°, 2 h		314						
	C (1 eq), rt, 12 h	I (100)	84						
	(EtO) ₃ SiH (2.3 eq), KF (1 eq), 100°, 2 h	 I (65) (80)	83, 80, 79						
	PMHS (1 eq), ZnCl ₂ (1 eq), Et ₂ O, rt, 24 h	I (65)	315						
	PhSiH ₃ (0.4 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE, O ₂ , rt	I (80)	367						
	B (1 eq), rt, 12 h	I (100)	84						
	PhMe ₂ SiH (1.3 eq), (Ph ₃ P)CuH (3 mol%), MeC ₆ H ₅ , 2 h	 I (100) (89)	317						
	Et ₃ SiH (1.0 eq), TMSOTf (0.1 eq), ROTMS (0.83 eq), CH ₂ Cl ₂ , 0° to rt	 I (100)	341						
		<div style="display: flex; align-items: center;"><div style="margin-right: 10px;">R</div><table><tr><td><i>n</i>-C₆H₁₃</td><td>(88)</td></tr><tr><td><i>i</i>-Pr</td><td>(73)</td></tr><tr><td><i>t</i>-Bu</td><td>(63)</td></tr></table></div>	<i>n</i> -C ₆ H ₁₃	(88)	<i>i</i> -Pr	(73)	<i>t</i> -Bu	(63)	
<i>n</i> -C ₆ H ₁₃	(88)								
<i>i</i> -Pr	(73)								
<i>t</i> -Bu	(63)								

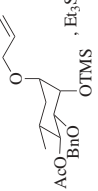
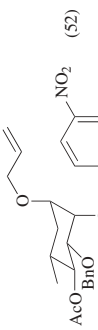
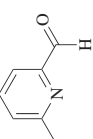
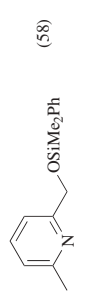
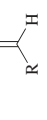







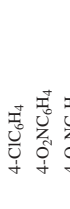
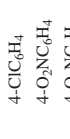



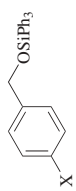
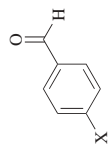
		341
		345
		91
		116
		314
		
		
		

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{7,8}$ 	R^2_3SiH (1.2 eq), $n-Bu_4NClO_4$ (0.1 eq), $LiClO_4$ (0.1 eq), CH_2Cl_2 , electrolysis	$R^1-CH_2-O-CH_2-R^1$	333
R^1	R^2_3Si		
Ph	Et_3Si	(91.0)	
Ph	$PhMe_2Si$	(95.7)	
4-MeC ₆ H ₄	$PhMe_2Si$	(94.5)	
4-ClC ₆ H ₄	$PhMe_2Si$	(86.3)	
$n-C_6H_{13}$	$PhMe_2Si$	(91.8)	
$Ar-C(=O)-H$	Me_3SiH (1.25 eq), $TMSI$ (0.3 eq), $t-BuOTMS$ (1.25 eq), $n-C_3H_7$, -78° to rt, 5-6 h	$Ar-CH_2-OBu-t$	338
		Ar	
		Ph (67)	
		4-FC ₆ H ₄ (77)	
		4-MeC ₆ H ₄ (71)	
		3-MeC ₆ H ₄ (87)	
		2-MeC ₆ H ₄ (21)	
		2-MeOC ₆ H ₄ (64)	
		Ar	
	$Ph-CH_2-CH_2-CH_2-OTHP$, Et_3SiH (2.2 eq), $TMSOTf$ (10 mol%), MeCN, 0° , 1 h	$Ar-CH_2-CH_2-CH_2-CH_2-Ph$	340
		Ph (98)	
		4-ClC ₆ H ₄ (95)	
		4-O ₂ NC ₆ H ₄ (90)	
		4-MeOC ₆ H ₄ (90)	
		4-MeC ₆ H ₄ (98)	
		X	
		H (81)	115
		Me (82)	
		Cl (81)	
		NO ₂ (96)	





C₇₋₉



R
Ph
4-MeOC ₆ H ₄
4-NCC ₆ H ₄
4-O ₂ NC ₆ H ₄



R ¹
<i>n</i> -C ₆ H ₁₃
Ph
Ph
Ph
Ph
(<i>E</i>)-PhCH=CH
(<i>E</i>)-PhCH=CH

Et₃SiH (1.2 eq), TMSCl (50 mol%),
InCl₃ (20 mol%), R²STMS (1.2 eq),
CH₂Cl₂, rt, 5 h



R ¹	R ²
Ph	Et (87)
Ph	<i>i</i> -Pr (83)
Ph	Ph (82)
BnCH ₂	Et (81)
<i>n</i> -C ₈ H ₁₇	Et (78)

1. Et₃SiH, BF₃, CH₂Cl₂
2. BF₃•OEt₂, rt

Time	I	II
11 min	(—)	(52)
10 min	(0)	(100)
10 min	(100)	(0)
5 min	(100)	(0)

Ph₃SiH, (C₆F₅)₃B (2 mol%),
MeC₆H₅, rt



Ar
Ph (87)
4-MeC ₆ H ₄ (82)
4-ClC ₆ H ₄ (81)
4-O ₂ NC ₆ H ₄ (96)

R³₃SiH (1.2 eq), R²OTMS,
(*n*-Bu)₄NClO₄ (0.1 eq),
LiClO₄ (0.1 eq), CH₂Cl₂, electrolysis



R ²	R ³ ₃ Si
Bn(CH ₂) ₂	PhMe ₂ Si (81.9)
Bn(CH ₂) ₂	PhMe ₂ Si (98.8)
H ₂ C=CHCH ₂	Et ₃ Si (71.2)
HC≡CCH ₂	Et ₃ Si (95.0)
(CH ₂) ₂ OTMS	PhMe ₂ Si (63.2) ^b
H ₂ C=CHCH ₂	Et ₃ Si (51.1)
HC≡CCH ₂	Et ₃ Si (49.8)

426

I

116

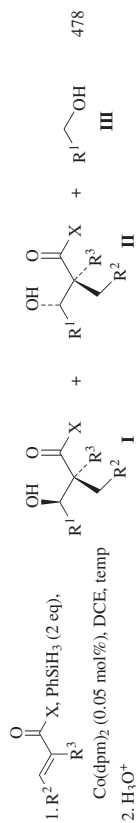
333

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

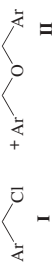
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-9} $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{H} \end{array}$	Et_3SiH (1.3 eq), BiCl_3 (0.11 eq), R^2OH , CH_2Cl_2 , rt	$\text{R}^1-\text{CH}_2-\text{O}-\text{R}^2$	332
R^1	R^2		
$c\text{-C}_6\text{H}_{11}$	BnCH_2CH_2	(77)	
$c\text{-C}_6\text{H}_{11}$	BnCH_2CHMe	(70)	
Ph	$\text{HO}_2\text{C}(\text{CH}_2)_{11}$	(38)	
Ph	Et	(74)	
Ph	$n\text{-C}_9\text{H}_{19}$	(95)	
Ph	Bn	(80)	
Ph	BnCH_2CH_2	(93)	
Ph	BnCH_2CHMe	(82)	
Bn	BnCH_2CH_2	(61)	
BnCH_2	BnCH_2CH_2	(73)	
BnCH_2	BnCH_2CHMe	(69)	
$n\text{-C}_7\text{H}_{15}$	BnCH_2CH_2	(63)	
$n\text{-C}_7\text{H}_{15}$	BnCH_2CHMe	(64)	

C₇₋₈

R ¹	
Ph	
(<i>E</i>)-PhCH=CH	
BnCH ₂	
Ph	
(<i>E</i>)-PhCH=CH	
Ph	
(<i>E</i>)-PhCH=CH	
(<i>E</i>)-PhCH=CH	
BnCH ₂	
Ar	
Ph	
2-ClC ₆ H ₄	
4-ClC ₆ H ₄	
4-O ₂ NC ₆ H ₄	
3-HOC ₆ H ₄	
4-MeC ₆ H ₄	
4-MeOC ₆ H ₄	
4-MeO ₂ CC ₆ H ₄	



R ²	R ³	X	Temp	Time	I + II	I:II	III
H	H	NMe ₂	20°	2 h	(95)	80:20	(3)
H	H	NMe ₂	20°	4 h	(96)	72:28	(trace)
H	H	NMe ₂	20°	6 h	(90)	70:30	(trace)
Me	H	NMe ₂	50°	3 h	(72)	70:30	(10)
Me	H	NMe ₂	20°	4 h	(68)	72:28	(12)
H	Me	NMe ₂	20°	5 h	(50)	—	(31)
H	Me	NMe ₂	20°	4 h	(70)	—	(14)
H	H	OMe	20°	20 h	(80)	50:50	(10)
H	H	OMe	20°	20 h	(62)	50:50	(14)

HMe₂SiOSiMe₂H (1.0 eq),TMSCl (1.57 eq), SO₂Cl₂ (1.37 eq),ZnI₂ (cat.)

314

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-9} $\begin{array}{c} O \\ \\ Ar-C-H \end{array}$	$HMe_2SiOSiMe_2H$ (1.0 eq), $TMSCl$ (1.5 eq), $LiBr$ (1.7 eq), $MeCN$, 80°	$Ar-CH_2-Br$ + $Ar-CH_2-O-CH_2-Ar$ <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> I $Ar-CH_2-Br$ </div> <div style="text-align: center;"> II $Ar-CH_2-O-CH_2-Ar$ </div> </div>	314, 356
Ar	Time	I II	
Ph	30 min	(94)	(—)
2- ClC_6H_4	15 min	(64)	(—)
4- ClC_6H_4	20 min	(90)	(—)
3- HOC_6H_4	45 min	(77)	(23)
4- MeC_6H_4	20 min	(97)	(—)
4- $MeO_2CC_6H_4$	80 min	(80)	(20)
4- $MeOC_6H_4$	15 min	(84)	(—)
O $\begin{array}{c} \\ Ar-C-H \end{array}$	$HMe_2SiOSiMe_2H$ (1.0 eq), I_2 (0.6 eq), CH_2Cl_2 , -5°	I $Ar-CH(I)-R$	357
Ar	Time		
Ph	10 min	(80)	
2- ClC_6H_4	10 min	(72)	
3- HOC_6H_4	5 min	(87)	
4- MeC_6H_4	10 min	(70)	
4- $MeOC_6H_4$	10 min	(66)	
4- NCC_6H_4	15 min	(75)	
4- $MeO_2CC_6H_4$	45 min	(75)	
2,4- $Me_2C_6H_3$	8 min	(83)	
O $\begin{array}{c} \\ R-C-H \end{array}$	Et_3SiH (1.2 eq), $BiBr_3$, (10-30 mol%), τ	$R-CH_2-O-CH_2-R$	
		R Time	
		Ph	<5 min (84)
		4- ClC_6H_4	<5 min (93)
		4- BrC_6H_4	<5 min (89)
		2- $MeOC_6H_4$	8 h (83)
		4- $MeO_2CC_6H_4$	<5 min (85)
		4- $Me_2NCC_6H_4$	20 h (0)
		$n-C_7H_{15}$	2 h (88)

Ar	Ar
Ph	Ph
Ph	Ph
Ph	Ph
4-(TMS)C ₆ H ₄	4-(TMS)C ₆ H ₄
4-(TMS)C ₆ H ₄	4-(TMS)C ₆ H ₄
4- <i>r</i> -BuC ₆ H ₄	4- <i>r</i> -BuC ₆ H ₄
4- <i>r</i> -BuC ₆ H ₄	4- <i>r</i> -BuC ₆ H ₄

R₃SiH, SnCl₂ (cat.)

R ₃ Si	Time
Et ₃ Si	180 min
(<i>n</i> -Bu) ₃ Si	120 min
Et(<i>i</i> -C ₃ H ₇) ₂ Si	120 min
Et ₃ Si	180 min
(<i>n</i> -Bu) ₃ Si	120 min
Et ₃ Si	180 min
(<i>n</i> -Bu) ₃ Si	60 min

R₃SiH (x eq), NiCl₂ (cat.), 90 min

Ar	R ₃ Si	x
Ph	Et ₃ Si	1.0
Ph	(<i>n</i> -Bu) ₃ Si	1.0
Ph	Et(<i>i</i> -C ₃ H ₇) ₂ Si	1.0
4-(TMS)C ₆ H ₄	Et ₃ Si	2.0
4-(TMS)C ₆ H ₄	(<i>n</i> -Bu) ₃ Si	2.0
4- <i>r</i> -BuC ₆ H ₄	Et ₃ Si	2.0
4- <i>r</i> -BuC ₆ H ₄	(<i>n</i> -Bu) ₃ Si	2.0
4- <i>r</i> -BuC ₆ H ₄	Et ₃ Si	1.0

PMHS (3 eq), Triton-B (2 mol%),
THF, rt

Ar	Ar
Ph	Ph
4-NCC ₆ H ₄	4-NCC ₆ H ₄
4-MeC ₆ H ₄	4-MeC ₆ H ₄
3,4,5-(MeO) ₃ C ₆ H ₂	3,4,5-(MeO) ₃ C ₆ H ₂

Ar-OSiR₃

(12.1)
(27.5)
(28.3)
(11.5)
(19.8)
(15.1)
(71.8)



I	II
(23.4)	(58.2)
(36.5)	(36.0)
(37.6)	(39.2)
(10.1)	(80.2)
(20.1)	(40.3)
(52.9)	(—)
(53.1)	(21.6)
(21.7)	(47.3)

278

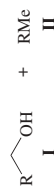
344

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.															
C_{7-10} <div>$\begin{array}{c} \text{O} \\ \parallel \\ \text{Ar}-\text{C}-\text{H} \end{array}$</div>	PMHS (3 eq), TBAF (2 mol%), THF, rt	<div>$\begin{array}{c} \text{Ar}-\text{CH}_2-\text{OH} \\ \hline \text{Ar} \end{array}$<div><div>Ph</div><div>4-ClC₆H₄</div><div>4-O₂NC₆H₄</div><div>2-OHCC₆H₄</div><div>3,4-[OCH₂O]C₆H₃</div><div>4-MeC₆H₄</div><div>3,4,5-(MeO)₃C₆H₂</div></div><div>(92) (88) (91) (79) (95) (98) (96)</div></div>	278															
<div>$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$</div>	(EtO) ₃ SiH (1.1 eq), MF (1 eq)	<div>$\begin{array}{c} \text{R}-\text{CH}_2-\text{OH} \end{array}$</div>	79															
C_{7-11} <div>$\begin{array}{c} \text{O} \\ \parallel \\ \text{Ar}-\text{C}-\text{H} \end{array}$</div>	<table><thead><tr><th>MF</th><th>Temp</th><th>Time</th></tr></thead><tbody><tr><td>KF</td><td>100°</td><td>2 h</td></tr><tr><td>CsF</td><td>80°</td><td>8 h</td></tr><tr><td>KF</td><td>rt</td><td>24 h</td></tr><tr><td>KF</td><td>rt</td><td>1 h</td></tr></tbody></table> <div>$\begin{array}{c} \text{R} \\ \hline 4\text{-O}_2\text{NC}_6\text{H}_4 \\ 4\text{-MeCONHC}_6\text{H}_4 \\ (E)\text{-PhCH=CH} \\ \text{Me}_2\text{C=CH(CH}_2)_2\text{CH(Me)CH}_2 \end{array}$<div>(80) (80) (95) (80)</div></div>	MF	Temp	Time	KF	100°	2 h	CsF	80°	8 h	KF	rt	24 h	KF	rt	1 h	<div>$\begin{array}{c} \text{Ar}-\text{CH}_2-\text{OSiEt}_3 \\ \hline \text{Ar} \end{array}$<div>Ph</div><div>4-<i>i</i>-BuC₆H₄</div><div>4-(TMS)C₆H₄</div><div>(71.9) (72.5) (56.5)</div></div>	344
MF	Temp	Time																
KF	100°	2 h																
CsF	80°	8 h																
KF	rt	24 h																
KF	rt	1 h																
C_{7-12} <div>$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$</div>	Et ₃ SiH (x eq), acid (y eq), solvent, 28°	<div>$\begin{array}{c} \text{R}-\text{CH}_2-\text{OH} \\ \text{I} \end{array} + \begin{array}{c} \text{R}-\text{CH}_2-\text{O}-\text{CH}_2-\text{R} \\ \text{II} \end{array} + \begin{array}{c} \text{Other} \\ \text{III} \end{array}$</div>	313															

$$\text{C}_{7-11} \quad \begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{R} \end{array}$$



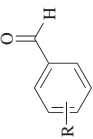
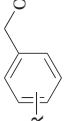
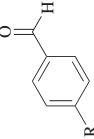
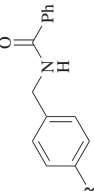
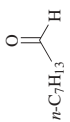
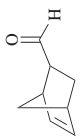
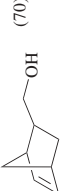
1. BF_3 (gas), CH_2Cl_2 , 0°
2. Et_3SiH (x eq), 0°

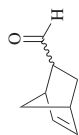


	x	Time	I	II
1	18	11 min	(—)	(52)
	10	10 min	(—)	(68)
2	1.5	5 min	(100)	(—)
	10	10 min	(—)	(45)
3	2	10 min	(—)	(100)
	3	10 min	(100)	(—)
4	1.5	10 min	(92)	(—)

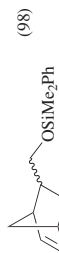
R	Ph
4-ClC ₆ H ₄	
4-O ₂ NC ₆ H ₄	
4-MeC ₆ H ₄	
4-MeOC ₆ H ₄	
4-NCC ₆ H ₄	
<i>n</i> -C ₁₀ H ₂₁	

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 	$[HSi(OEt)_4]K$, THF, 0°	R  Time Ph 3 h (90) 4-BrC ₆ H ₄ 4 h (84) n-C ₇ H ₁₅ 4 h (80)	288
C_{7-14} 	Ph_2MeSiH (2.5 eq), $(Ph_3P)CuH$ (3 mol%), MeC ₆ H ₅	R  Time 2-Br 30 min (95) 4-Br 45 min (98) 4-O ₂ N 30 min (89) 4-MeO 120 min (92) 4-TsO 60 min (89) 3-BnO 120 min (97)	317
C_{7-23} 	Et_3SiH (3 eq), TFA (2.9 eq), PhCONH ₂ (3 eq), MeC ₆ H ₅ , 120° , 18 h	R  Time F (96) CO ₂ H (96) CO ₂ Me (91) OAc (75) OBn (90) OTBS (46) OTBDPS (91)	326
C_8 	Et_3SiH (1.1 eq), $BF_3 \cdot OEt_2$ (2.0 eq), rt	n-C ₇ H ₁₃ O C ₇ H ₁₃ ⁿ (66) + n-C ₇ H ₁₃ OH (34) I (81)	74
	L , THF, 0° , 2 h (EtO) ₃ SiH (1.1 eq), KF (1 eq), rt, 1 h	I (81) 	96 80

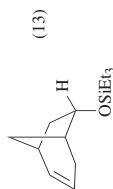


PhMe₂SiH (1.3 eq),
(Ph₃P)CuH (3 mol%), MeC₆H₅, 2 h

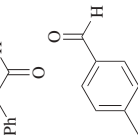


317

Et₃SiH (5 eq), Ni(cod)₂ (0.2 eq),
PPh₃ (0.4 eq), THF, 55°, 17 h



349

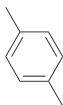


Me₂CiSiH (1.2 eq), In(OH)₃ (5 mol%),
CHCl₃, 60°, 5.5 h



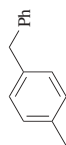
331

R₃SiH (x eq), TFA (y eq), solvent



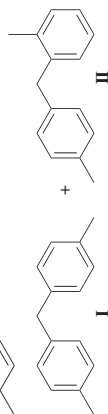
73

R ₃ Si	x	y	Solvent	Time
Et ₃ Si	2.2	8.0	TFA	11 h (20)
PhMe ₂ Si	2.2	8.0	TFA	13 h (46)
PhMe ₂ Si	2.5	5.0	TFA	15 min (52)
Et ₃ Si	6.0	5.0	MeCN	170 h (50)
Et ₃ Si	2.2	6.7	MeCN	180 h (43)
Et ₃ Si	6.0	5.0	MeNO ₂	54 h (61)
Et ₃ Si	2.2	5.0	CCl ₄	100 h (50)
Et ₃ Si	6.0	5.0	CCl ₄	336 h (66)



(60)

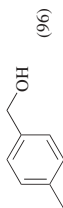
PMHS, TMSOTf (cat.), C₆H₆,
reflux, 2.5 h



I + II (80), **II** = 90:10

314

PMHS, TMSOTf (cat.),
MeC₆H₅, reflux, 0.5 h



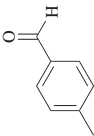
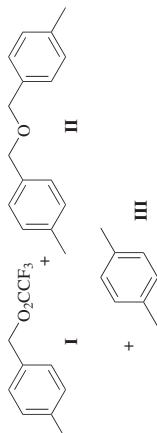
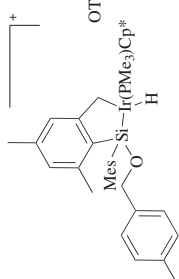
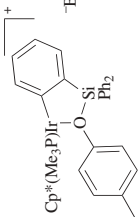
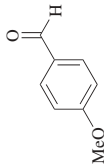
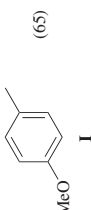
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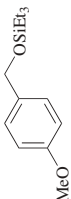
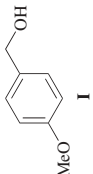
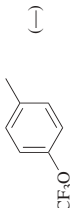
314

F, 0°, 2 h

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TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.																																			
 C ₈	Et ₃ SiH (6 eq), TFA (5 eq), CCl ₄ , rt	 I + III → II	73																																			
		<table><tr><th>Time</th><th>I</th><th>II</th><th>III</th><th>Other</th></tr><tr><td>16 h</td><td>(31)</td><td>(56)</td><td>(13)</td><td>(0)</td></tr><tr><td>22 h</td><td>(31)</td><td>(46)</td><td>(23)</td><td>(0)</td></tr><tr><td>45 h</td><td>(42)</td><td>(30)</td><td>(26)</td><td>(2)</td></tr><tr><td>89 h</td><td>(38)</td><td>(12)</td><td>(39)</td><td>(11)</td></tr><tr><td>209 h</td><td>(9)</td><td>(0)</td><td>(61)</td><td>(30)</td></tr><tr><td>336 h</td><td>(0)</td><td>(0)</td><td>(66)</td><td>(34)</td></tr></table>	Time	I	II	III	Other	16 h	(31)	(56)	(13)	(0)	22 h	(31)	(46)	(23)	(0)	45 h	(42)	(30)	(26)	(2)	89 h	(38)	(12)	(39)	(11)	209 h	(9)	(0)	(61)	(30)	336 h	(0)	(0)	(66)	(34)	
Time	I	II	III	Other																																		
16 h	(31)	(56)	(13)	(0)																																		
22 h	(31)	(46)	(23)	(0)																																		
45 h	(42)	(30)	(26)	(2)																																		
89 h	(38)	(12)	(39)	(11)																																		
209 h	(9)	(0)	(61)	(30)																																		
336 h	(0)	(0)	(66)	(34)																																		
	[Cp [*] (Me ₃ P)Ir(SiMes ₂ (H))][OTf] (1 eq), CD ₂ Cl ₂	 (85)	745																																			
	[Cp [*] (Me ₃ P)Ir(η ₂ -SiPh ₂ C ₆ H ₄ (H))] ⁺ [(C ₆ F ₅) ₄ B] ⁻ , CH ₂ Cl ₂ , rt, 10 min	 (48)	745																																			
	PMHS (3 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 5-20 min	 I	354																																			

	R ₃ Si	x	Time		
I	Et ₃ Si	2.5	30 min	(76)	73
	PhMe ₂ Si	6.0	90 min	(80)	
	PhMe ₂ Si	6.0	30 min	(81)	
	Et ₃ Si	6.0	45 min	(83)	
					76
	<p>Et₃SiH (1.4 eq), TBAF (1.4 eq), MeCN, rt, 12 h</p>				
	<p>PMHS (2.5 eq), (Ph₃P)CuH (3 mol%), MeC₆H₅, 3 h</p>				317
					367
	<p>I (56)</p>				
	<p>PhSiH₃ (0.4 eq), Mn(dpm)₃ (3 mol%), <i>i</i>-PrOH, DCE, O₂, rt</p>				315
	<p>I (68)</p>				
	<p>PMHS (1 eq), ZnCl₂ (1 eq), Et₂O, rt, 24 h</p>				84
	<p>I (100)</p>				
	<p>C (1 eq), rt, 12 h</p>				
					414
	<p>Et₃SiH, TFA</p>				

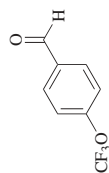
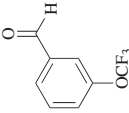
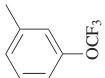
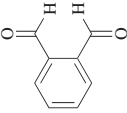
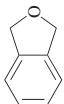
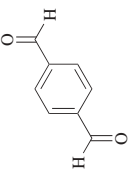
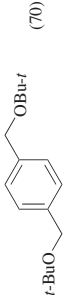
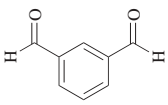
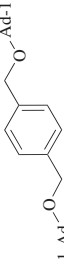
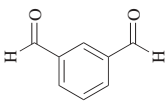
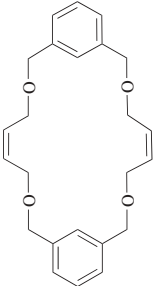
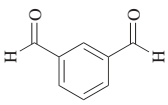



TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et ₃ SiH, TFA	 (—)	414
	TMSH (4 eq), TMSOTf (1.6 mol%), CH ₂ Cl ₂ , 0°, 4 h; rt, 2 h	 (99)	392
	TMSH (2.5 eq), TMSI (0.3 eq), <i>t</i> -BuOTMS (2.5 eq), <i>n</i> -C ₅ H ₁₂ , −78° to rt, 5–6 h	 (70)	338
	1-AdOTMS (2.5 eq), TMSH (2.5 eq), TMSI (0.3 eq), <i>n</i> -C ₅ H ₁₂ , −78° to rt, 5–6 h	 (78)	338
	(<i>Z</i>)-TMSOCH ₂ CH=CHCH ₂ OTMS, Et ₃ SiH (2.4 eq), BiBr ₃ (10 mol%), CH ₂ Cl ₂ /MeCN, −30° to 0°	 (<1)	343
	(<i>Z</i>)-TMSOCH ₂ CH=CHCH ₂ OTMS, Et ₃ SiH (1.2 eq), TMSOTf (10 mol%), CH ₂ Cl ₂ , −30° to 0°	 I (8) + others	343

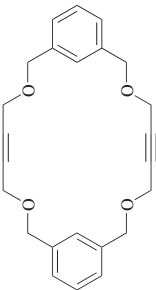

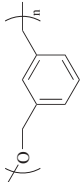
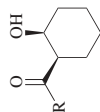
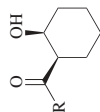

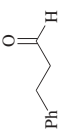
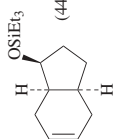
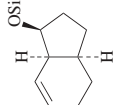

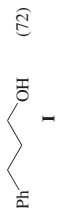
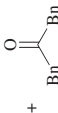
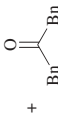



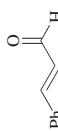





$\text{TMSOCH}_2\text{---CH}_2\text{OTMS}$, Et_3SiH (2.4 eq), BiBr_3 (10 mol%), $\text{CH}_2\text{Cl}_2/\text{MeCN}$, -30° to 0°		(7) + others	343															
$\text{TMSOCH}_2\text{---CH}_2\text{OTMS}$, Et_3SiH (2.4 eq), TMSOTf (10 mol%), CH_2Cl_2 , -30° to 0°		I (10) + others	343															
Et_3SiH (2 eq), TrClO_4 (10 mol%), CH_2Cl_2		I	<table><tr><th>Temp</th><th>Time</th><th>M_n</th></tr><tr><td>0°</td><td>0.25 h</td><td>6500 (52)</td></tr><tr><td>0°</td><td>6 h</td><td>10,400 (40)</td></tr><tr><td>-20°</td><td>0.25 h</td><td>8800 (58)</td></tr><tr><td>-50°</td><td>24 h</td><td>11,400 (54)</td></tr></table>	Temp	Time	M_n	0°	0.25 h	6500 (52)	0°	6 h	10,400 (40)	-20°	0.25 h	8800 (58)	-50°	24 h	11,400 (54)
Temp	Time	M_n																
0°	0.25 h	6500 (52)																
0°	6 h	10,400 (40)																
-20°	0.25 h	8800 (58)																
-50°	24 h	11,400 (54)																
R_3SiH (2 eq), Ph_3CClO_4 (10 mol %), CH_2Cl_2 , -20° , 1 h		I	<table><tr><th>R_3Si</th><th>M_n</th></tr><tr><td>Et_3Si</td><td>8600 (63)</td></tr><tr><td>$(n\text{-C}_6\text{H}_{13})_3\text{Si}$</td><td>5600 (24)</td></tr><tr><td>PhMe_2Si</td><td>9200 (63)</td></tr><tr><td>Ph_3Si</td><td>9900 (23)</td></tr></table>	R_3Si	M_n	Et_3Si	8600 (63)	$(n\text{-C}_6\text{H}_{13})_3\text{Si}$	5600 (24)	PhMe_2Si	9200 (63)	Ph_3Si	9900 (23)					
R_3Si	M_n																	
Et_3Si	8600 (63)																	
$(n\text{-C}_6\text{H}_{13})_3\text{Si}$	5600 (24)																	
PhMe_2Si	9200 (63)																	
Ph_3Si	9900 (23)																	
PhSiH_3 (1.2 eq), Co(dpm)_2 (5 mol%), rt		R	<table><tr><th>R</th><th>M_n</th></tr><tr><td>Me</td><td>(38)</td></tr><tr><td>$2\text{-C}_4\text{H}_9\text{O}$</td><td>(75)</td></tr><tr><td>$2\text{-C}_4\text{H}_9\text{S}$</td><td>(73)</td></tr><tr><td>Ph</td><td>(87)</td></tr><tr><td>$4\text{-F}_3\text{CC}_6\text{H}_5$</td><td>(72)</td></tr><tr><td>$2\text{-C}_{10}\text{H}_7$</td><td>(68)</td></tr></table>	R	M_n	Me	(38)	$2\text{-C}_4\text{H}_9\text{O}$	(75)	$2\text{-C}_4\text{H}_9\text{S}$	(73)	Ph	(87)	$4\text{-F}_3\text{CC}_6\text{H}_5$	(72)	$2\text{-C}_{10}\text{H}_7$	(68)	
R	M_n																	
Me	(38)																	
$2\text{-C}_4\text{H}_9\text{O}$	(75)																	
$2\text{-C}_4\text{H}_9\text{S}$	(73)																	
Ph	(87)																	
$4\text{-F}_3\text{CC}_6\text{H}_5$	(72)																	
$2\text{-C}_{10}\text{H}_7$	(68)																	
Et_3SiH (1 eq), TrClO_4 (5 mol%), CH_2Cl_2 , 0° , 5 min		$n\text{-C}_8\text{H}_{17}$ (88)	329															

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	Et_3SiH (5 eq), $\text{Ni}(\text{cod})_2$ (0.2 eq), PPh_3 (0.4 eq), THF, 30°, 10 h	 (44) +  (22)	349
	PMHS (3 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 5–20 min	 (90)	354
	PMHS (1 eq), ZnCl_2 (1 eq), Et_2O , rt, 24 h	 I (72)	315
 + 	$\text{Me}(\text{EtO})_2\text{SiH}$ (1.2 eq), KO_2CH (1 eq), DMF, 80°, 15 h	I +  II (83), I:II = 100:0	82
	Et_3SiH (1 eq), TrClO_4 (5 mol%), CH_2Cl_2 , 0°, 5 min	 (83)	329
	PhMe_2SiH (1.3 eq), $(\text{Ph}_3\text{P})\text{CuH}$ (3 mol%), MeC_6H_5 , 2 h	 (90)	317
	Et_3SiH (0.72 eq), H_2PtCl_6	 (—)	76
	Et_3SiH (1.5 eq), CsF (1.5 eq), MeCN , rt, 10 h	 I (—)	76
	PhMe_2SiH (1.2 eq), TBAF (2 eq), HMPA, rt, 0.5 h	 (100)	320
	EtO_3SiH (1.5 eq), HAP, rt, 2 h	 I +  II (70)	353

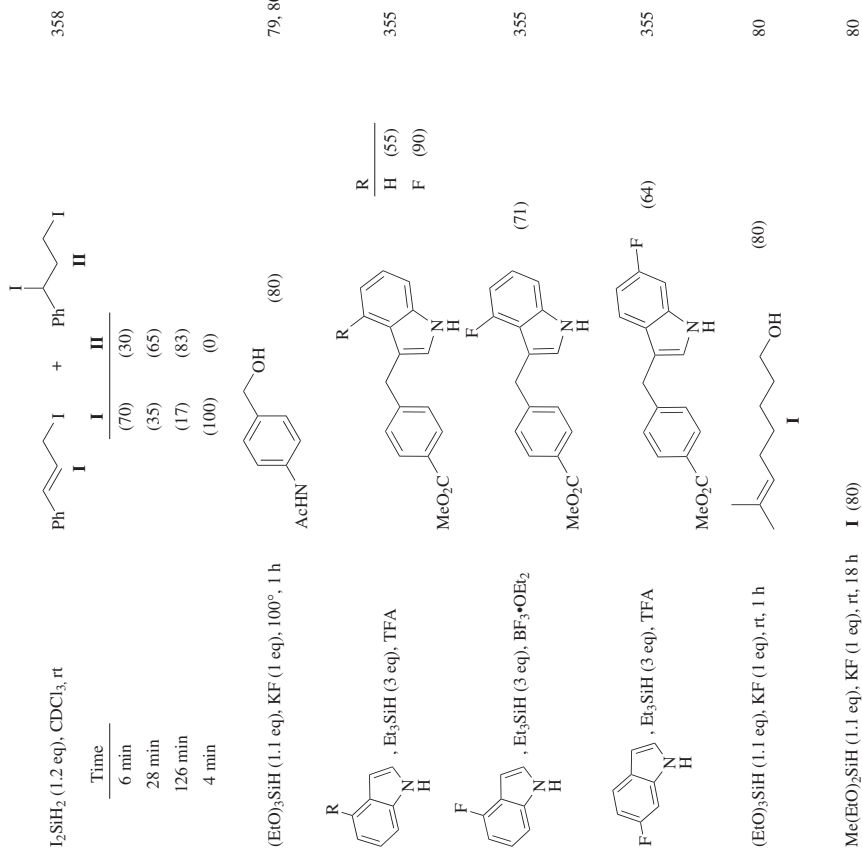


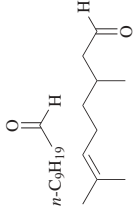

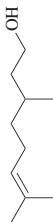
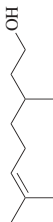
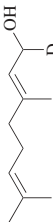

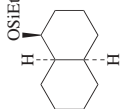
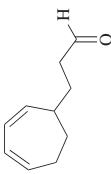
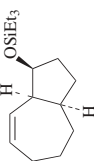
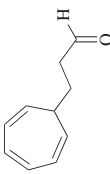
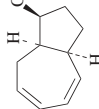


TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et ₃ SiH (3 eq), TFA (5 eq), 40-50°, 6 h	 (73)	351
	Et ₃ SiH, ZnCl ₂	n-C ₉ H ₁₉ O-C ₉ H ₁₉ -n (50)	330
	PhMe ₂ SiH (1.3 eq), (Ph ₃ P)CuH (3 mol%), MeC ₆ H ₅ , 2 h	 (93)	317
	Me(EtO) ₂ SiH (1.5 eq), KF (1 eq), DMF, 35°, 2.5 h	 (68)	82
	PMHS (2.5 eq), KF (1.25 eq), DMF, 30°, 0.75 h	 I (70)	82
	Ph ₂ SiD ₂ (1.1 eq), (Ph ₃ P) ₃ RhCl	 (92)	435
	Et ₃ SiH (5 eq), Ni(cod) ₂ (0.2 eq), PPh ₃ (0.4 eq), THF, 30°, 3 h	 (60)	349
	Et ₃ SiH (5 eq), Ni(cod) ₂ (0.2 eq), PPh ₃ (0.4 eq), THF, 30°, 4 h	 (81)	349
	Et ₃ SiH (5 eq), Ni(cod) ₂ (0.2 eq), PPh ₃ (0.4 eq), THF, 30°, 2 h	 (47)	349

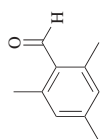
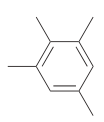
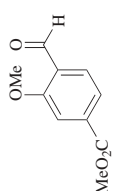
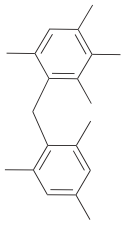
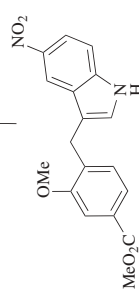
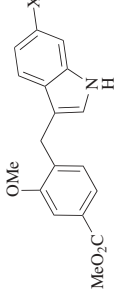
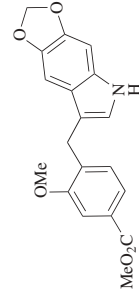
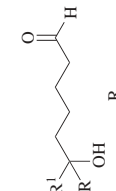
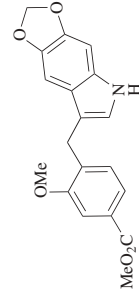
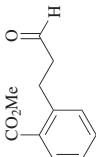
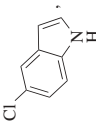
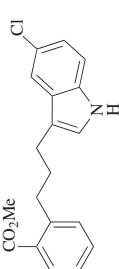
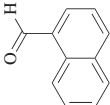
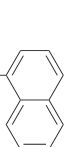
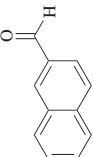
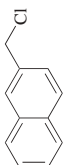





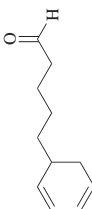
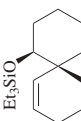
		Et_3SiH (2.2 eq), TFA (10.0 eq), rt, 15 min	73
		Et_3SiH , TFA, 30–40°	311
		O_2N $\text{BF}_3\cdot\text{OEt}_2$, Et_3SiH (3 eq), acid	355
		X $\text{BF}_3\cdot\text{OEt}_2$ (3 eq), TFA	355
		X Acid Cl TFA Cl $\text{BF}_3\cdot\text{OEt}_2$ (43) F $\text{BF}_3\cdot\text{OEt}_2$ (47)	355
		Et_3SiH (2 eq), $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , –78°, 1 h; 20°, 16 h	746
	R^1 R —(CH ₂) ₄ — —(CH ₂) ₅ — Ph Me Ph Et Ph Ph		

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	 , Et_3SiH (3 eq), TFA	 (55)	355
	Et_3SiH (1.1 eq), $(C_6F_5)_3B$ (5 mol%), CH_2Cl_2 , rt, 20 h	 (96)	282
	Me_2ClSiH (1.2 eq), $In(OH)_3$ (5 mol%), $CHCl_3$, rt, 2.5 h	 (92)	331
$n-C_{10}H_{21}CHO$	Et_3SiH (3.0 eq), $(C_6F_5)_3B$ (5 mol%), CH_2Cl_2 , rt, 20 h	 (96)	282
	$PhMe_2SiH$ (1.3 eq), $(Ph_3P)CuH$ (3 mol%), MeC_6H_5 , 2 h	 (95)	317
	Et_3SiH (5 eq), $Ni(cod)_2$ (0.2 eq), PPh_3 (0.4 eq), THF, 35°, 8 h	 (36)	349
	Et_3SiH (5 eq), $Ni(cod)_2$ (0.2 eq), PPh_3 (0.4 eq), THF, 55°, 10 h	 (30)	349

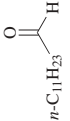

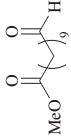
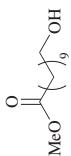
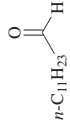
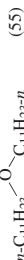
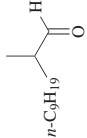

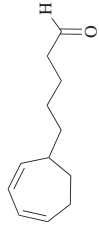
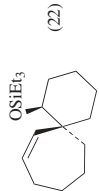
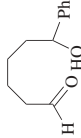
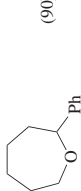
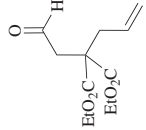
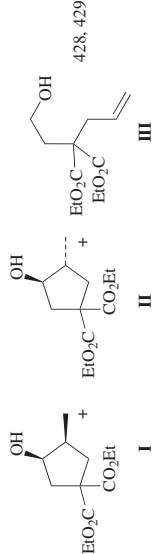
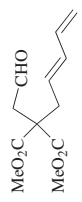
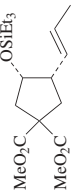
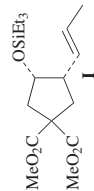
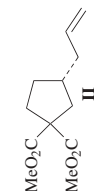

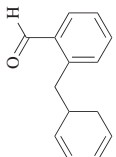
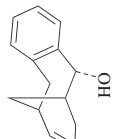
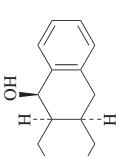
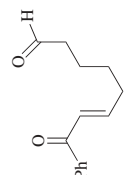
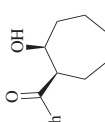
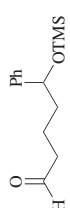



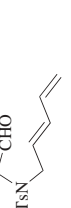
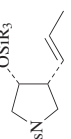
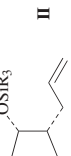
		Et_3SiH (3 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 20 h	(95)	281
		PMHS (1 eq), ZnCl_2 (1 eq), Et_2O , rt, 24 h	(70)	315
		Et_3SiH , ZnCl_2	(55)	330
		PhMe_2SiH (1.3 eq), $(\text{Ph}_3\text{P})\text{CuH}$ (3 mol%), MeC_6H_5 , 2 h	(92)	317
		Et_3SiH (5 eq), $\text{Ni}(\text{cod})_2$ (0.2 eq), PPh_3 (0.4 eq), THF, 45°, 34 h	(22)	349
		Ph_2MeSiH (2 eq), TMSOTf (1 eq), CH_2Cl_2 , 0°, 2 h	(90)	336
		Ph_2SiH_2 , $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ (10 mol%), PMe_3 (60 mol%), MeC_6H_5 , -20°	I + II: III = 99:1, I:II = 99:1, I (65)	428, 429

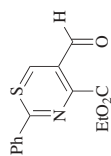
TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.				
C_{12} 	Et_3SiH (5 eq), $Ni(cod)_2$ (20 mol%), ligand (40 mol%), THF, rt, 12 h		348				
	Ligand	% ee					
	PPh_3	(84) 0					
	(<i>S</i>)-BINAP	(2) 0					
	(<i>R</i>)-H-MOP	(2) 16					
	(<i>S,R</i>)-PPFA	(3) 10					
	NMDPP	(2) (—)					
	118	(13) 3					
	R_3SiH (5 eq), 41 (20 mol%), $Ni(cod)_2$ (10 mol%), solvent, 5 h	 I +  II	348				
	R_3Si	Solvent	Temp	Time	I + II	I:II	% ee I
Et_3Si	THF	rt	5 h	(84)	4.3:1	2	47
<i>t</i> -BuMe ₂ Si	THF	rt	8 h	(83)	>50:1	16	—
(EtO) ₃ Si	THF	0°	5 h	(60)	12:1	46	33
Ph_3Si	THF	0°	2 h	(80)	1.7:1	47	53
Ph_2MeSi	THF	0°	2 h	(83)	1.2:1	27	78
$PhMe_2Si$	THF	0°	7 h	(82)	1.9:1	21	72
Ph_2MeSi	MeC ₆ H ₅	0°	3 h	(88)	1.7:1	17	77
Ph_2MeSi	DMF	0°	3 h	(87)	1.1:1	39	81
Ph_2MeSi	DMF	−20°	28 h	(73)	1.1:1.2	44	86
Ph_2MeSi	MeCN	−20°	24 h	(83)	1:1	40	85

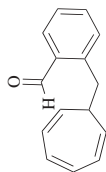
	<p>PhSiH₃ (1.2 eq), Co(dpm)₂ (5 mol%), rt</p>		461
<p>C₁₃</p>	<p>R₃SiH (5 eq), Ni(cod)₂ (10 mol%), 41 (20 mol%), DMF</p>		348
	<p>(EtO)₃SiH (5 eq), Ni(cod)₂ (10 mol%), 41 (20 mol%), MeCN, -30°, 10 h</p>		348
<p>C₁₃₋₁₄</p>	<p>Cl₃SiH (3 eq), (<i>n</i>-Pr)₃N (x eq), 1 h</p>		711

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

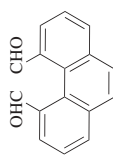
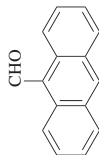
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.																		
	PMHS (1 eq), ZnCl ₂ (1 eq), Et ₂ O, rt, 24 h	THPO-CH ₂ -CH ₂ -(CH ₂) ₈ -OH (80)	315																		
	Et ₃ SiH (5 eq), Ni(cod) ₂ (0.2 eq), PPh ₃ (0.4 eq), THF, 55°, 8 h	 (34) +  (17)	349																		
	PhSiH ₃ (1.2 eq), Co(dpm) ₂ (5 mol%), 35°	 (35)	461																		
	1. SbCl ₅ , TMSCl, SnI ₂ , CH ₂ Cl ₂ , -78°, 30 min 2. Et ₃ SiH (1.5 eq), -23°, 2.5 h	 (76)	306																		
	1. TrSbCl ₆ (5-30 mol%), CH ₂ Cl ₂ , -78°, 30 min 2. Et ₃ SiH (1.5 eq), -23°, 2.5 h	 (90)	306																		
	R ₃ SiH (5 eq), Ni(cod) ₂ (10 mol%), 41 (20 mol %), solvent	 I +  II	348																		
<table><tr><th>R₃Si</th><th>Solvent</th><th>Time</th><th>I + II</th><th>I:II</th><th>% ee I:II</th></tr><tr><td>(EtO)₃Si</td><td>MeCN</td><td>6 h</td><td>(60)</td><td>4.6:1</td><td>48:41</td></tr><tr><td>Ph₂MeSi</td><td>DMF</td><td>42 h</td><td>(22)</td><td>1:2.4</td><td>10:67</td></tr></table>				R ₃ Si	Solvent	Time	I + II	I:II	% ee I:II	(EtO) ₃ Si	MeCN	6 h	(60)	4.6:1	48:41	Ph ₂ MeSi	DMF	42 h	(22)	1:2.4	10:67
R ₃ Si	Solvent	Time	I + II	I:II	% ee I:II																
(EtO) ₃ Si	MeCN	6 h	(60)	4.6:1	48:41																
Ph ₂ MeSi	DMF	42 h	(22)	1:2.4	10:67																



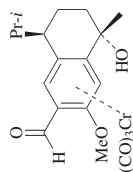
C₁₅



C₁₆



C₁₉

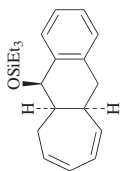


Et₃SiH, TFA

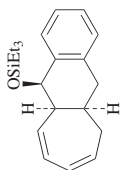
(40)

747

Et₃SiH (5 eq), Ni(cod)₂ (0.2 eq),
PPh₃ (0.4 eq), THF, 35°, 16 h



(15) +



349

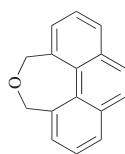
PhMe₂SiH (1.3 eq),
(Ph₃P)CuH (3 mol%), MeC₆H₅, 2 h



(96)

317

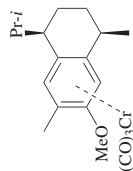
Et₃SiH (8 eq), TMSOTf (1 eq),
CH₂Cl₂, rt, 45 min



(92)

339

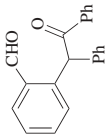
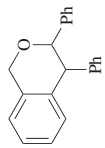
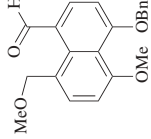
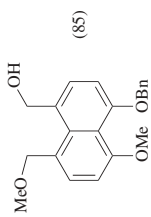
Et₃SiH (6 eq), TFA (9 eq), 60°, 4.5 h



(82)

352

TABLE 11. ORGANOSILANE REDUCTION OF ALDEHYDES (Continued)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (8 eq), TMSOTf (1 eq), CH_2Cl_2 , rt, 45 min	 (59)	339
	PMHS (2.5 eq), $(\text{Ph}_3\text{P})\text{CuH}$ (3 mol%), MeC_6H_5 , 1.5 h	 (85)	317

^a The yield was determined by NMR spectroscopy.^b The product associated with this yield is $(\text{PhCH}_2\text{OCH}_2)_2$.

TABLE 12. ORGANOSILANE REDUCTION OF KETONES





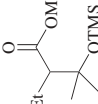
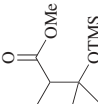

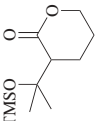











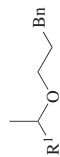
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (1.1–1.2 eq), HCO_2H , HOAc , KU-1 , 55° , 5 h	 (95)	208
	Et_3SiH (1 eq), ZnCl_2 , 100° , 24 h	 (78)	382
	Ph_2SiH_2 (1 eq), $[\text{Cp}^*(\text{Me}_3\text{P})\text{Ir}(\eta^2\text{-SiPh}_2\text{C}_6\text{H}_4)(\text{H})]^+$ $[(\text{C}_6\text{F}_5)_4\text{B}]^-$ (5 mol%), CD_2Cl_2 , rt, 3 h	 (33) + $\text{Ph}_2\text{Si}(\text{OPr-}i)_2$ (40)	745
	$(E)\text{-CH}_3\text{CH=CHCO}_2\text{Me}$, TMSh (1.3 eq), $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ (0.009 mol%), rt	 (89)	473
	$\text{CH}_2=\text{CHCO}_2\text{Me}$, TMSh (1.3 eq), $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ (0.009 mol%), rt	 (24)	473
	TMSh (1.3 eq), $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ (0.009 mol%), rt	 (34)	473
	Ph_2SiH_2 , $(\text{Ph}_3\text{P})_3\text{RuCl}_2$ or $(\text{Ph}_3\text{P})_3\text{RhCl}$ (5×10^{-4} M)	 (—)	744
	Ph_2SiH_2 (1.3 eq), $(\text{Ph}_3\text{P})_4\text{RhH}$ (0.4 mol%), CH_2Cl_2 , rt, 12 h	 (80)	374

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₋₆	<div>$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$</div>	Et ₃ SiH (x eq), acid, H ₂ O (y eq), MeCN, 28°	<div>$\begin{array}{c} \text{OH} \\ \\ \text{R}^1-\text{CH}-\text{R}^2 \end{array} \quad (100)$</div>	313
	<div>$\begin{array}{c} \text{R}^1 \\ \hline \text{R}^2 \end{array}$</div>	x Acid y Time		
	Me	1.1 HCl 0 2.5 h		
	<i>t</i> -Bu	1.25 H ₂ SO ₄ 11 1.5 h		
	—(CH ₂) ₅ —	1.1 HCl 0 2.5 h		
C ₃₋₈	—(CH ₂) ₅ —	1.25 H ₂ SO ₄ 11 1.5 h		
	<div>$\begin{array}{c} \text{R}^1 \\ \hline \text{R}^2 \end{array}$</div>	Et ₃ SiH (x eq), TFA (y eq), solvent, 28°	<div>$\begin{array}{c} \text{OH} \\ \\ \text{R}^1-\text{CH}-\text{R}^2 \end{array} \quad \text{I}$ + <div>$\begin{array}{c} \text{R}^1 \\ \\ \text{R}^2-\text{O}-\text{CH}-\text{R}^1 \\ \quad \\ \text{R}^2 \quad \text{R}^2 \end{array} \quad \text{II}$ + <div>$\begin{array}{c} \text{R}^1 \\ \\ \text{R}^2-\text{O}-\text{CH}-\text{R}^1 \\ \quad \\ \text{R}^2 \quad \text{R}^2 \end{array} \quad \text{III}$</div></div> + other</div>	313
	Me	x y Solvent Time	<div>$\begin{array}{c} \text{I} \quad \text{II} \quad \text{III} \\ \hline (32) \quad (68) \quad (0) \\ (25) \quad (75) \quad (0) \\ (42) \quad (58) \quad (0) \\ (5) \quad (80) \quad (15) \\ (0) \quad (12) \quad (88) \\ (7) \quad (93) \quad (0) \end{array}$</div>	
	—(CH ₂) ₅ —	1.1 20 none 1.3 h		
	—(CH ₂) ₅ —	1.1 20 none 1.5 h		
C ₃₋₁₀	Ph	1.0 3.0 none 1.0 h		
	CH ₂ Br	2.5 20 none 0.25 h		
	CH ₂ Br	2.5 20 none 44 h		
	4-O ₂ NC ₆ H ₄	6.0 10 CCl ₄ 22 h		
	Me			
C ₃₋₁₀	<div>$\begin{array}{c} \text{R}^1 \\ \hline \text{R}^2 \end{array}$</div>	Et ₃ SiH, HClO ₄ , MeCN, rt	<div>$\begin{array}{c} \text{OH} \\ \\ \text{R}^1-\text{CH}-\text{R}^2 \end{array} \quad (—)$</div>	380
	Me			
	Ph			
	4-ClC ₆ H ₄			
	Me			
C ₃₋₁₀	Et			
	Ph			
	4-MeC ₆ H ₄			
	Me			
	4-NCC ₆ H ₄			
C ₃₋₁₀	Ph			
	<i>n</i> -Pr			

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-13} <div>  </div>	PMHS (10% xs), (Bu ₂ (AcO)Sn) ₂ O (2 mol%), EtOH, reflux	<div>  </div>	316
<div> $\begin{array}{c} R^1 \\ \hline R^2 \\ \hline \end{array}$ </div>		(100)	
Me		(65)	
H ₂ C=CH		(81)	
Ph		(80)	
Ph			
C_4 <div>  </div>	Et ₃ SiH (1 eq), EtOH (2 eq), TFA (4 eq), 50-60°	<div>  </div>	327
	Et ₃ SiH (1 eq), HC(OEt) ₃ (1 eq), EtOH, HCl, TFA (3 eq), 50-60°, 6-8 h	I (60)	327
<div>  </div>	Et ₃ SiH (2.5 eq), (Ph) ₃ PtCl (0.5 mol%), 70°, 3 h	<div>  </div>	411
C_{4-10} <div>  </div>	Et ₃ SiH (1.2 eq), R ³ OTMS (1.2 eq), BiBr ₃ (10-30 mol%), rt	<div>  </div>	343
<div> $\begin{array}{c} R^1 \\ \hline R^2 \\ \hline \end{array}$ </div>	<div> $\begin{array}{c} R^3 \\ \hline \text{Time} \end{array}$ </div>		
HOCH ₂	Bn	1 h	(—)
H ₂ C=CH	Bn	20 h	(trace)
Me	Bn	<5 min	(89)
—(CH ₂) ₅ —	Bn	1 h	(96)
n-C ₆ H ₁₃	Bn	20 h	(trace)
Ph	2-octyl	1 h	(88)
Me			
Bn			
Et			

C₄₋₈R₃SiH (1.2 eq), BnCH₂CH₂OTMS,(n-Bu)₄NClO₄ (0.1 eq),LiClO₄ (0.1 eq), CH₂Cl₂, electrolysis

333

R₃SiPhMe₂SiEt₃SiPhMe₂Si

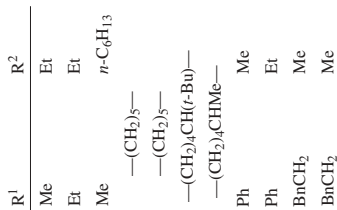
(95)

(87)

(80)

C₄₋₁₀Et₃SiH (5 eq), **209** (3 mol%),CuCl (3 mol%), NaOBu-*t* (20 mol%),MeC₆H₅, rt

412



(93)

(82)

(96)

(73)

(83)

(35)

(95)

(94)

(95)

(73)

(100)

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄₋₁₂ $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$	Et ₃ SiH (5 eq), 210 (3 mol%), CuCl (3 mol%), NaOBu- <i>t</i> (20 mol%), MeC ₆ H ₅ , rt	$\begin{array}{c} \text{OSiEt}_3 \\ \\ \text{R}^1-\text{CH}-\text{R}^2 \end{array}$	412
R ¹	R ²		
Me	Et	(80)	
Et	Et	(91)	
<i>n</i> -C ₆ H ₁₃	Me	(82)	
<i>n</i> -C ₉ H ₁₉	Me	(86)	
—(CH ₂) ₅ —		(93)	
—(CH ₂) ₄ CHMe—		(91)	
<i>c</i> -C ₃ H ₅		(87)	
Ph	Me	(94)	
BnCH ₂	Me	(85)	
Ph	Et	(96)	
1-C ₁₀ H ₇	Me	(93)	
C ₅ $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	Et ₃ SiH (1.2 eq), 208 (0.2 mol%), rt, 15 min	$\begin{array}{c} \text{OSiEt}_3 \\ \\ \text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array} \quad (93) \quad + \quad \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \quad (5)$	377
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	TMSH (1.1 eq), TMSI (5 mol%), CH ₂ Cl ₂ , 0°	$\begin{array}{c} \text{C}-\text{C}-\text{C} \\ \quad \quad \\ \text{C} \quad \text{C} \quad \text{O} \quad \text{C}-\text{C}-\text{C} \\ \quad \quad \quad \quad \\ \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \end{array}$ (—), dr = 100:0 (R.R:S:S)	334

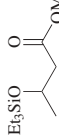
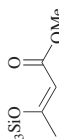

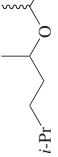
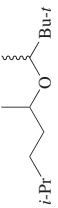


















	Et_3SiH (2.2 eq), 208 (0.2 mol%), rt, 168 h	 (77) + $\text{Et}_3\text{SiOCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (14)	377																																			
	Et_3SiH (2 eq), TMSOTf (0.1 eq), CH_2Cl_2 , rt, 2 h	 (100) ^a	334																																			
	Ph_2SiH_2 (1.3 eq), $(\text{Ph}_3\text{P})_4\text{RhH}$ (0.3 mol%), CH_2Cl_2 , rt, 4 h	 (86)	374																																			
	Et_3SiH (1 eq), $(\text{Ph}_3\text{P})_3\text{RhCl}$	 I +  II (80), I:II = 81:19	411																																			
	PhMe_2SiH (1.2 eq), TBAF (5 mol%), HMPA, 0°, 12 h	 I +  II (95), I:II = 71:29	320																																			
C_{5-7} 	R_3SiH (1 eq), Cp_2TiPh_2 (1.6 mol%)		748																																			
<table><tr><th>R^1</th><th>R^2</th><th>R_3Si</th><th>Temp</th><th>Time</th></tr><tr><td>Et</td><td>Et</td><td>Ph_2HSi</td><td>120°</td><td>11 h</td></tr><tr><td>Et</td><td>Et</td><td>PhMeHSi</td><td>90°</td><td>8 h</td></tr><tr><td>—(CH₂)₄—</td><td></td><td>Ph_2HSi</td><td>120°</td><td>11 h</td></tr><tr><td>Me</td><td><i>n</i>-C₃H₉</td><td>Ph_2HSi</td><td>120°</td><td>5 h</td></tr><tr><td>Me</td><td><i>n</i>-C₄H₉</td><td>Ph_2HSi</td><td>120°</td><td>11 h</td></tr><tr><td>Me</td><td><i>n</i>-C₅H₉</td><td>Ph_2HSi</td><td>120°</td><td>20 h</td></tr></table>				R^1	R^2	R_3Si	Temp	Time	Et	Et	Ph_2HSi	120°	11 h	Et	Et	PhMeHSi	90°	8 h	—(CH ₂) ₄ —		Ph_2HSi	120°	11 h	Me	<i>n</i> -C ₃ H ₉	Ph_2HSi	120°	5 h	Me	<i>n</i> -C ₄ H ₉	Ph_2HSi	120°	11 h	Me	<i>n</i> -C ₅ H ₉	Ph_2HSi	120°	20 h
R^1	R^2	R_3Si	Temp	Time																																		
Et	Et	Ph_2HSi	120°	11 h																																		
Et	Et	PhMeHSi	90°	8 h																																		
—(CH ₂) ₄ —		Ph_2HSi	120°	11 h																																		
Me	<i>n</i> -C ₃ H ₉	Ph_2HSi	120°	5 h																																		
Me	<i>n</i> -C ₄ H ₉	Ph_2HSi	120°	11 h																																		
Me	<i>n</i> -C ₅ H ₉	Ph_2HSi	120°	20 h																																		

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₅₋₁₇ <div></div>	PMHS, Sn(OTf) ₂ (10 mol%), L-histidine (10 mol%), MeOH, rt, 12-14 h	<div></div>	385	
R ¹	R ²			
CO ₂ Et	CF ₃	(75)		
2-C ₄ H ₃ S	CO ₂ Et	(98)		
Ph	Me	(98)		
Ph	CO ₂ Me	(99)		
4-O ₂ NC ₆ H ₄	CO ₂ Me	(98)		
Ph	CO ₂ Et	(99)		
4-MeOC ₆ H ₄	CO ₂ Me	(99)		
4-MeC ₆ H ₄	CO ₂ Me	(96)		
1-C ₁₀ H ₇	CO ₂ Me	(98)		
2-C ₁₀ H ₇	CO ₂ Me	(96)		
Ph	CH ₂ - <i>N</i> -phthalimide	(89)		
4-ClC ₆ H ₄	CH ₂ - <i>N</i> -phthalimide	(50)		
4-O ₂ NC ₆ H ₄	CH ₂ - <i>N</i> -phthalimide	(98)		
4-MeC ₆ H ₄	CH ₂ - <i>N</i> -phthalimide	(88)		
C ₆ <div></div>	TMSH (1.1 eq), TMSI (5 mol%), CH ₂ Cl ₂ , 0°	<div></div>	(-), dr = 100:0 (R,S,S,R)	334
	<div></div> TMSI (5 mol%), TMSH (1.1 eq), CH ₂ Cl ₂ , 0°	<div></div>	(-), dr = 54:45	334
	<div></div> Ph TMSI (5 mol%), TMSH (1.1 eq), CH ₂ Cl ₂ , 0°	<div></div>	(-), dr = —	334

	<i>i</i> -Pr TMSI (5 mol%), CH ₂ Cl ₂ , 0°		(-), dr = 50:50	334
	(EtO) ₃ SiH (1 eq), CsF, rt, 1 h		(80)	80
	(EtO) ₃ SiH (1 eq), KF, 100°, 24 h		I (0)	80
	H , 0°, 5 h		I (92)	93
	Et ₃ SiH (1.1 eq), H ₂ SO ₄ , H ₂ O, MeCN, 28°, 65 h		(67)	313
	TMSH (4 eq), TMSOTf (1.6 mol%), CH ₂ Cl ₂ , 0°, 4 h; rt, 2 h		I + II (85), I:II = 50:50	390
	Ph ₂ SiH ₂ (1.0 eq), Cp ₂ Ti(PPh ₃) ₂ , MeC ₆ H ₅ , -20°		I + II (85), I:II = 50:50	428
	Ph ₂ SiH ₂ (1.0 eq), Cp ₂ Ti(PPh ₃) ₂ , MeC ₆ H ₅ , -20°		I + II (85), I:II = 50:50	429
	Ph ₂ SiH ₂ , Cp ₂ Ti(PMe ₃) ₂ (10 mol%), PMe ₃ (60 mol%), MeC ₆ H ₅ , -20°		I + II:III = 80:1; I:II = 3:2, I+II (72)	429
	Et ₃ SiH (1.2 eq), 208 (0.2 mol%), rt, 19 h		(98)	377

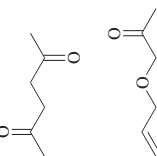

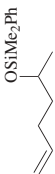
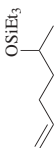
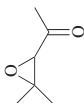
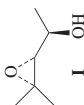
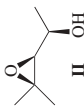


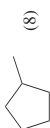




TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMe ₂ SiH (1.2 eq), TBAF (5 eq), HMPA, rt, 12 h	 (57)	320
	Et ₃ SiH (3 eq), 209 (3 mol%), NaOBu- <i>t</i> (20 mol%), MeC ₆ H ₅ , rt, 1 h	 (97)	412
	Me(EtO) ₂ SiH (1.5 eq), KF (1 eq), DMF, 60°, 5 h	I (85)	82, 83
	PMHS (1.5 eq), KF•2H ₂ O (1 eq), DMSO, 60°, 1.5 h	I (65)	82
	(EtO) ₃ SiH (2.3 eq), CsF (1 eq), 0°, 15 min	I (90)	83
	Me(EtO) ₂ SiH (2.3 eq), KF (1 eq), DMF, 60°, 5 h	I (85)	82, 83
	PhMe ₂ SiH (1.2 eq), TBAF (5 mol%), HMPA, 0°, 12 h	 I (85) +  II (100), I:II = 65:35	320
	Et ₃ SiH (3 eq), AlCl ₃ (0.5 eq), HCl, CH ₂ Cl ₂ , rt, 5 h	 I (60) +  (8)	136
	Et ₃ SiH (1.5 eq), CF ₃ SO ₃ H (4 eq), CH ₂ Cl ₂ , 0° to rt, 2 h	 I (22) ^b +  II (75) ^b	420
	1. Et ₃ SiH (2 eq), BF ₃ , CH ₂ Cl ₂ , 0°, 1.5 min 2. H ₂ O	I (82) + II (0)	1

1. Et₃SiH (4 eq), BF₃, CH₂Cl₂, 0°, 30 min **I** (0) + **II** (90)

2. H₂O

(EtO)₃SiH (1 eq), KF, 100°, 12 h **II** (75)

(*i*-Pr)₂Si(OPr-*i*)H, SnCl₄, CH₂Cl₂, 0°, 3 h **II** (92)

Silane (1.5 eq), salt (1 eq), DMF **II**

Silane Temp Time



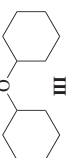
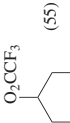
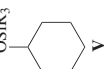
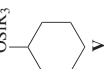
Me(EtO) ₂ SiH	KF	80°	1 h	(77)
PMHS	KF	60°	1.5 h	(70)
PMHS	KF·2H ₂ O	30°	1 h	(64)
Me(EtO) ₂ SiH	KO ₂ CH	80°	5 h	(75)
PMHS	KO ₂ CH	80°	23 h	(—)

R₃SiH (1.2 eq), [Rh(C₂H₄)₂]₂ (0.5 mol%), **II**

ligand (2 mol%), C₆H₆, rt

R ₃ SiH	Ligand	Time	
Et ₃ SiH	P(tm-tp) ₃	21 h	(81)
Et ₃ SiH	P(tp) ₃	21 h	(36)
Et ₃ SiH	PPh ₃	21 h	(13)
PhMe ₂ SiH	P(tm-tp) ₃	20 h	(97)
PhMe ₂ SiH	P(tp) ₃	20 h	(37)
PhMe ₂ SiH	PPh ₃	20 h	(27)
PhMe ₂ SiH	P(tm-tp) ₃	6 h	(95)
PhMe ₂ SiH	P(tp) ₃	6 h	(65)
PhMe ₂ SiH	PPh ₃	6 h	(9)
PhMe ₂ SiH	P(2-C ₄ H ₅ O) ₃	3 h	(22)
PhMe ₂ SiH	P(<i>o</i> -tol) ₃	3 h	(32)
PhMe ₂ SiH	PMes ₃	3 h	(25)
PhMe ₂ SiH	PEt ₃	3 h	(<2)
PhMe ₂ SiH	P(C ₆ H ₁₁ - <i>c</i>) ₃	3 h	(<2)
PhMe ₂ SiH	P(Bu- <i>i</i>) ₃	3 h	(31)

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 			
	L , THF, 0°, 2 h	 II (80)	96
	H , 0°, 5 h	II (100)	93
	G , rt, 2 h	II (95)	93
	Et ₃ SiH (1.3 eq), NH ₄ F (1.3 eq), TFA (5 eq), -30°, 2 h	 II + III (—), II:III = 95:5	135
	Et ₃ SiH (1.1 eq), BF ₃ •OEt ₂ (2.0 eq), rt	II (94) + III (6)	74
	Et ₃ SiH (2 eq), TMSOTf (0.1 eq), CH ₂ Cl ₂ , rt, 2 h	III (100) ⁹²	334
	TMSH (1.1 eq), TMSI (5 mol%), CH ₂ Cl ₂ , 0-15°, rt, 2 h	III (88)	334
	Et ₃ SiO(EtHSiO) ₁₀ SiEt ₃ (0.2 mol%), TFA (4 eq), CHCl ₃ , 50°, 10 h	 III (20) + IV (55)	136
	Et ₃ SiO(EtHSiO) ₁₀ SiEt ₃ (0.2 mol%), TFA (4 eq), CHCl ₃ , 50°, 10 h	 III (20) + IV (55)	136
	R ₃ SiH, acid	 + III	353

R ₃ Si	Acid	Amount ^c	Time	V	III
Et ₃ Si	Fe-mont	0.2 g	0.5 h	(7)	(81)
Et ₃ Si	CF ₃ SO ₃ H	0.1 mmol	0.5 h	(4)	(80)
Et ₃ Si	CF ₃ SO ₃ H	1.1 mmol	0.3 h	(67)	(4)
PhMe ₂ Si	Fe-mont	0.2 g	1.5 h	(0)	(84)
(EtO) ₃ Si	Fe-mont	0.2 g	20 h	(0)	(0)
Et ₃ Si	Na-mont	0.2 g	47 h	(0)	(0)
Et ₃ Si	SiO ₂	0.2 g	21 h	(0)	(0)

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III + IV

n-BuSiH₃ (0.5 eq), TFA (x eq)





x	Temp	Time	III	IV
6.0	55°	3.5 h	(38)	(62)
2.5	55°	1.5 h	(47)	(53)
3.0	rt	24 h	(49)	(51)
6.0	0°	3.5 h	(60)	(40)
3.0	0°	24 h	(67)	(33)
3.0	-15°	25 h	(82)	(18)
2.5	-15°	72 h	(90)	(10)

III (90) + IV (10)

313



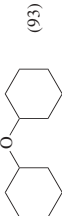

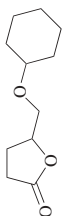
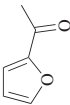
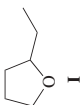
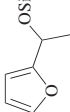
n-BuSiH₃ (0.5 eq),
TFA (2.5 eq), -15°, 72 h

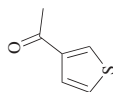
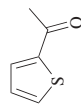
TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																		
 C_6	Et_3SiH (5 eq), $CuCl$ (3 mol%), $NaOBu-t$ (20 mol%), ligand (3 mol%), MeC_6H_5 , rt	 V	412																		
	<table><tr><th>Ligand</th><th>Time</th></tr><tr><td>210</td><td>2 h</td></tr><tr><td>211</td><td>2 h</td></tr><tr><td>213</td><td>8 h</td></tr><tr><td>212</td><td>8 h</td></tr><tr><td>216</td><td>2 h</td></tr><tr><td>215</td><td>8 h</td></tr><tr><td>214</td><td>24 h</td></tr><tr><td>none</td><td>24 h</td></tr></table>	Ligand	Time	210	2 h	211	2 h	213	8 h	212	8 h	216	2 h	215	8 h	214	24 h	none	24 h	(99) (80) (92) (35) (99) (38) (3) (0)	
	Ligand	Time																			
	210	2 h																			
	211	2 h																			
	213	8 h																			
	212	8 h																			
	216	2 h																			
	215	8 h																			
	214	24 h																			
none	24 h																				
Et_3SiH (1 eq), $ZnCl_2$, 95° , 48 h	V (87)		382																		
TBSH (3 eq), TBSOTf (0.01 eq), rt, 2 h	 (90)		392																		
R_3SiH (1.5 eq), Fe-mont, CH_2Cl_2 <table><tr><th>R_3Si</th><th>Temp</th><th>Time</th></tr><tr><td>Et_3Si</td><td>rt</td><td>1 h</td></tr><tr><td>$PhMe_2Si$</td><td>40°</td><td>6 h</td></tr><tr><td>$(EtO)_3Si$</td><td>40°</td><td>11 h</td></tr></table>	R_3Si	Temp	Time	Et_3Si	rt	1 h	$PhMe_2Si$	40°	6 h	$(EtO)_3Si$	40°	11 h	 (79) (—) (—)	324							
R_3Si	Temp	Time																			
Et_3Si	rt	1 h																			
$PhMe_2Si$	40°	6 h																			
$(EtO)_3Si$	40°	11 h																			

Et ₃ SiH (1.1 eq), MeOH, TFA, 28°		(88)	328
Et ₃ SiH (1.1 eq), EtOH, TFA, 28°		(68)	328
Et ₃ SiH (1.1 eq), EtOH, H ₂ SO ₄ , 28°	I	I (44)	328
Et ₃ SiH (1 eq), EtOH (3 eq), TFA (5 eq), 50-60°	I (16)		327
Et ₃ SiH (1 eq), HC(OEt) ₃ (1 eq), EtOH, HCl, TFA (3 eq), 50-60°, 6-8 h	I (72)		327
TMSH (1.1 eq), TMSI (5 mol%), EtOTMS (1 eq), CH ₂ Cl ₂ , 0-15°, rt, 2 h	I (91)		334
Et ₃ SiH (1 eq), HC(OEt) ₃ (1 eq), EtOH, TFA, 50-60°, 6-8 h	I (55)		327
Et ₃ SiH (1 eq), TMSOTf (0.1 eq), ROTMS (0.83 eq), CH ₂ Cl ₂ , -78° to -30°			341
$\begin{array}{c} \text{R} \\ \hline \text{Bn} \\ c\text{-C}_6\text{H}_{11} \\ t\text{-Bu} \end{array}$	(100)		
	(95)		
	(35)		

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

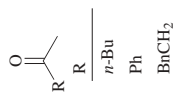
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
<div>C₆</div> <div></div>	Et ₃ SiH, TMSOTf, TMSI, <i>n</i> -C ₈ H ₁₇ OTMS, CH ₂ Cl ₂ , 0°, 2 h		334																																				
	TMSH (1.1 eq), TMSI (5 mol%), <i>c</i> -C ₆ H ₁₁ OTMS (1 eq), CH ₂ Cl ₂ , 0-15°; rt, 2 h	 (93)	334																																				
	 TMSOTf (0.1 eq), CH ₂ Cl ₂ , 0° to rt	 (93)	341																																				
<div></div>	Et ₃ SiH (10 eq), TFA (x eq), BF ₃ •OEt ₂ (y eq), 20°	 I	211																																				
	<table><tr><th>x</th><th>y</th><th>Time</th></tr><tr><td>30</td><td>0</td><td>5 min</td></tr><tr><td>30</td><td>0</td><td>30 min</td></tr><tr><td>30</td><td>0</td><td>1 h</td></tr><tr><td>30</td><td>0</td><td>2 h</td></tr><tr><td>30</td><td>0</td><td>20 h</td></tr><tr><td>50</td><td>0</td><td>5 min</td></tr><tr><td>50</td><td>0</td><td>30 min</td></tr><tr><td>50</td><td>0</td><td>1 h</td></tr><tr><td>50</td><td>0</td><td>2 h</td></tr><tr><td>28</td><td>0.6</td><td>5 min</td></tr><tr><td>28</td><td>0.6</td><td>1 h</td></tr></table>	x	y	Time	30	0	5 min	30	0	30 min	30	0	1 h	30	0	2 h	30	0	20 h	50	0	5 min	50	0	30 min	50	0	1 h	50	0	2 h	28	0.6	5 min	28	0.6	1 h	(17) (31) (46) (52) (65) (34) (67) (70) (79) (80) (80)	
x	y	Time																																					
30	0	5 min																																					
30	0	30 min																																					
30	0	1 h																																					
30	0	2 h																																					
30	0	20 h																																					
50	0	5 min																																					
50	0	30 min																																					
50	0	1 h																																					
50	0	2 h																																					
28	0.6	5 min																																					
28	0.6	1 h																																					
	PhMe ₂ SiH (1.1 eq), CsF (13.4 mol%), 18-C-6 (6.7 mol%), CH ₂ Cl ₂ , rt, 10 h	 (61)	346, 347																																				



C₆₋₉

Et₃SiH (1.2 eq), TMSCl (50 mol%),
InCl₃ (20 mol%), R³STMS (1.2 eq),
CH₂Cl₂, rt, 5 h

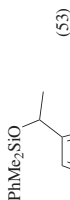
R ¹	R ²
—(CH ₂) ₅ —	
Ph	H
Ph	H
Ph	<i>i</i> -Pr
Ph	H
BnCH ₂	H
Ph	H
<i>n</i> -C ₈ H ₁₇	Me



I (70)



(45)



(53)



426

(93)

(87)

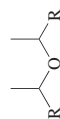
(83)

(82)

(81)

(98)

(78)



Et₃SiH (1.3 eq), BCl₃ (0.11 eq),
CH₂Cl₂, rt, 3 h

(29)

(trace)

(50)

332

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆₋₁₃ $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$	R ₃ SiH (1.5 eq), catalyst, n-C ₇ H ₁₆ , >90°	$\begin{array}{c} \text{R}^2 \\ \\ \text{R}^1-\text{C}-\text{OSiR}_3 \end{array}$	353
R ¹	R ₃ Si	Catalyst	Time
—(CH ₂) ₅ —	(EtO) ₃ Si	HAp	1 h
—(CH ₂) ₅ —	(EtO) ₃ Si	CaO	2 h
—(CH ₂) ₅ —	PhMe ₂ Si	CaO	8 h
—(CH ₂) ₅ —	Et ₃ Si	CaO	8 h
—(CH ₂) ₅ —	(EtO) ₃ Si	CaO	2 h
n-C ₆ H ₁₃	(EtO) ₃ Si	HAp	1 h
n-C ₈ H ₁₇	(EtO) ₃ Si	CaO	2 h
Ph	(EtO) ₃ Si	HAp	5 h
Ph	(EtO) ₃ Si	HAp	20 h
Ph	PhMe ₂ Si	HAp	23 h
Ph	Et ₃ Si	CaO	7 h
Ph	(EtO) ₃ Si	Ca(OH) ₂	21 h
Ph	(EtO) ₃ Si	CaF ₂	21 h
PhCH=CH	(EtO) ₃ Si	HAp	3 h
Ph	(EtO) ₃ Si	HAp	1 h
Ph	(EtO) ₃ Si	CaO	1 h

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$$

C₆₋₁₀

$$\begin{array}{c} \text{OH} \\ | \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$$

I

$$\begin{array}{c} \text{R}^1-\text{C}-\text{R}^2 \\ | \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$$

II

1. BF₃ (gas), CH₂Cl₂, 0°

2. Et₃SiH (x eq), 0°

R ¹	R ²	x	Time	I	II
—	—	2	1.5 min	(82)	(—)
—	—	4	30 min	(—)	(90)
—	—	2.2	60 min	(—)	(88)
—	—	4	3 min	(100)	(—)
—	—	3	10 min	(100)	(—)
—	—	3.3	60 min	(—)	(80)
—	—	2.2	60 min	(—)	(100)

C_{6,10}

332



Et₃SiH (1.3 eq), BiCl₃ (0.11 eq),
R³OH, CH₂Cl₂, rt

R ¹	R ²	R ³
—	—	BnCH ₂ CH ₂
Ph	Me	BnCH ₂ CH ₂
BnCH ₂	Me	Et

(75)

(29)

(24)

C_{6,11}

79



R₃SiH (1.1 eq), CsF (1 eq)

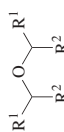
R ¹	R ²	R ₃ Si	Temp	Time
H ₂ C=C(CH ₂) ₂	Me	(EtO) ₃ Si	0°	15 min
Ph	MeCHBr	(EtO) ₃ Si	70°	30 min
Me	PhNHCOCH ₂	(EtO) ₃ Si	rt	10 h
Ph	MeO ₂ C(CH ₂) ₂	Me(EtO) ₂ Si	rt	2.5 min
<i>i</i> -PrO ₂ C(CH ₂) ₂	<i>i</i> -PrO ₂ C	(EtO) ₃ Si	0°	30 min

Et₃SiH (1.2 eq), BiBr₃ (10-30 mol%), rt

R ¹	R ²	Time
—	—	2 h
Ph	Me	20 h
BnCH ₂	Et	2 h
Ph	Ph	24 h

C_{6,13}

343



(72)

(trace)

(61)

(trace)

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₁₃ $\text{R}^1\text{C}(\text{O})\text{R}^2$	Ph ₂ SiH ₂ (0.5 eq), salt	$\text{R}^1\text{C}(\text{OSiPh}_2\text{H})\text{R}^2 \quad \text{I} \quad + \quad \left(\text{R}^1\text{C}(\text{R}^2)\text{OSiPh}_2 \right)_2 \quad \text{II}$	319
R ¹ R ²	Salt Temp Time	I II	
—(CH ₂) ₅ —	HCO ₂ K 100° 24 h	(70) (0)	
Ph Me	HCO ₂ K 180° 4 h	(25) (0)	
Ph Me	KF 100° 4 h	(40) (0)	
Ph Ph	KF 100° 24 h	(30) (0)	
Ph Ph	KF 150° 13 h	(0) (30)	
—(CH ₂) ₅ —	KF 100° 15 h	(70) (0)	
Ph Me	CsF rt 5 min	(0) (85)	
Ph Ph	CsF rt 30 min	(0) (100)	
—(CH ₂) ₅ —	CsF rt 15 min	(0) (99)	
Ph Me	BnMe ₂ NF rt 5 min	(0) (90)	
Ph Ph	BnMe ₂ NF rt 5 min	(0) (95)	
—(CH ₂) ₅ —	BnMe ₂ NF rt 10 min	(0) (85)	
	(MeO) ₃ SiH (1.3 eq), LiOCMe ₂ CMe ₂ OLi (2.4 eq), Et ₂ O, rt	$\text{R}^1\text{C}(\text{OH})\text{R}^2$	91
R ¹ R ²	Time		
2-C ₄ H ₉ O Me	15 h	(68)	
n-C ₈ H ₁₇ Me	15 h	(81)	
—(CH ₂) ₅ —	15 h	(83)	
—(CH ₂) ₆ —	15 h	(76)	
Ph Me	20 h	(97)	
4-BrC ₆ H ₄ Me	15 h	(94)	
Ph Et	15 h	(93)	
Ph Ph	15 h	(79)	
2-tetralone	15 h	(86)	

(EtO)₃SiH, catalyst, solvent, 90°

R ¹	R ²
Ph	—(CH ₂) ₅ —
Me	Ph
Ph	Ph
Ph	EtO
<i>n</i> -C ₃ H ₁₁	MeO
Me	PhCH=CH
—(CH ₂) ₅ —	
—(CH ₂) ₅ —	
—(CH ₂) ₅ —	
Ph	Ph
Ph	Ph
Me	Ph
Me	Ph
Ph	Ph
Me	Ph
Me	Ph
Me	Ph



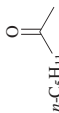
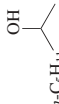
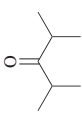
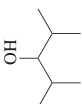

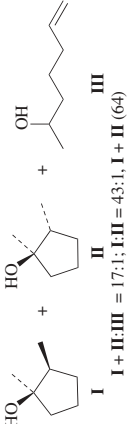
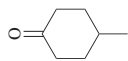
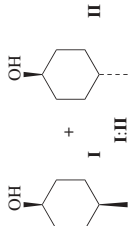
Catalyst	Solvent	Time
HAp	<i>n</i> -C ₇ H ₁₆	1 h
HAp	<i>n</i> -C ₇ H ₁₆	1 h
HAp	<i>n</i> -C ₇ H ₁₆	5 h
HAp	<i>n</i> -C ₇ H ₁₆	20 h
HAp	<i>n</i> -C ₇ H ₁₆	24 h
HAp	<i>n</i> -C ₇ H ₁₆	3 h
CaO	<i>n</i> -C ₇ H ₁₆	2 h
CaO	MeC ₆ H ₅	3 h
CaO	CH ₂ Cl ₂	2 h
CaO	<i>n</i> -C ₇ H ₁₆	1 h
CaO	MeC ₆ H ₅	14 h
CaO	<i>n</i> -C ₇ H ₁₆	17 h
CaO	MeC ₆ H ₅	13 h
MgO	<i>n</i> -C ₇ H ₁₆	15 h
Mg(OH) ₂	<i>n</i> -C ₇ H ₁₆	20 h
Ca(OH) ₂	<i>n</i> -C ₇ H ₁₆	21 h
CaF ₂	<i>n</i> -C ₇ H ₁₆	21 h

Et₃SiH (x eq), catalyst, rt

Catalyst	x	Time
Fe-mont	1.1	0.5 h
CF ₃ SO ₃ H	1.1	0.5 h
Fe-mont	2.2	4 h
Fe-mont	2.2	60 h
Sn-mont	2.2	2 h
CF ₃ SO ₃ H	2.2	24 h
CF ₃ SO ₃ H	2.2	24 h
Sn-mont/Et ₃ N	2.2	2 h

R ¹	R ²
Ph	—(CH ₂) ₅ —
Me	Me
Ph	Ph
Ph	Ph
Ph	Ph
Ph	Ph
Ph	Ph



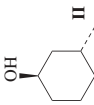
TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	H₂ , 0°, 5 h	 <i>n</i> -C ₅ H ₁₁ OH (90)	93
	H₂ , 0°, 30 h	 (50)	93
	Ph ₂ SiH ₂ (1.0 eq), Cp ₂ Ti(PPh ₃) ₂ , MeC ₆ H ₅ , -20°	 I + II:III = 17:1; I:II = 43:1, I + II (64)	428, 429
	R ₃ SiH (1.1 eq), acid catalyst (1 eq), 0° to rt, 24 h	 I + II	72, 381, 384
	R₃Si	Acid Catalyst	
	<i>n</i> -BuH ₂ Si	BF ₃ •OEt ₂	19:81
	Et ₂ HSi	BF ₃ •OEt ₂	39:61
	Et ₃ Si	BF ₃ •OEt ₂	60:40
	<i>n</i> -BuH ₂ Si	H ₂ SO ₄	18:82
	Et ₂ HSi	H ₂ SO ₄	26:74
	Et ₃ Si	H ₂ SO ₄	35:65
	Et ₃ Si	TFA (6.8 eq)	36:64
	(<i>n</i> -Bu) ₃ Si	H ₂ SO ₄	25:75
	(<i>i</i> -C ₃ H ₁₁) ₃ Si	TFA (6.7 eq)	33:67
	(<i>c</i> -C ₃ H ₉) ₃ Si	TFA (7 eq)	48:52
	(<i>i</i> -Bu) ₃ Si	TFA (7 eq)	56:44
	(<i>s</i> -Bu) ₃ Si	TFA (7 eq)	58:42
	(<i>t</i> -Bu) ₃ Si	TFA (7.2 eq)	67:33

Et ₃ SiH (1.1 eq), acid, rt	Acid		I:II		74
	BF ₃ •OEt ₂		60:40		
	TFA		36:64		
	H ₂ SO ₄		35:65		278
Silane, catalyst	I + II (>90)				367
	I:II				
	Silane				
	Catalyst				
	PMHS		18:82		
	Triton-B		16:84		386
	TBAF		16:84		
	(TMSO) ₃ SiH		16:84		
	(TMSO) ₃ SiH		14:86		386
	TBAF				
PhSiH ₃ (0.4 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE, O ₂ , rt	I + II (98), I:II 13:1				386
(t-Bu) ₂ SiH ₂ (1 eq), TFA (6.6 eq), rt, 20h	I (5) + II (62) + III (33)				386
(t-Bu) ₂ MeSiH (1 eq), TFA (6.6 eq), rt, 20 h	I (5) + II (62) + III (33)				278
Silane, catalyst	I + II (>90)				278
	I:II				
	Silane				
	Catalyst				
	PMHS		33:67		
	Triton-B		30:70		278
	TBAF		15:85		
	(TMSO) ₃ SiH		7:93		
	(TMSO) ₃ SiH				278
	TBAF				

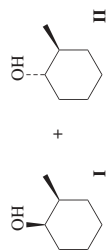


TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																													
<div>C₇ </div>	<div>R_3SiH (1.1 eq), acid catalyst (1 eq), 0° to rt, 24 h</div>	<div> + </div>	72, 381, 384																																													
	<table><tr><th>R_3Si</th><th>Acid Catalyst</th><th>I:II</th></tr><tr><td><i>n</i>-BuH₂Si</td><td>BF₃•OEt₂</td><td>76:24</td></tr><tr><td>Et₂HSi</td><td>BF₃•OEt₂</td><td>52:48</td></tr><tr><td>Et₃Si</td><td>BF₃•OEt₂</td><td>33:67</td></tr><tr><td><i>n</i>-BuH₂Si</td><td>H₂SO₄</td><td>81:19</td></tr><tr><td>Et₂HSi</td><td>H₂SO₄</td><td>71:29</td></tr><tr><td>Et₃Si</td><td>H₂SO₄</td><td>61:39</td></tr><tr><td>Et₃Si</td><td>TFA (6.8 eq)</td><td>58:42</td></tr><tr><td>(<i>n</i>-Bu)₃Si</td><td>H₂SO₄</td><td>65:35</td></tr><tr><td>(<i>n</i>-C₆H₁₃)₃Si</td><td>H₂SO₄</td><td>68:32</td></tr><tr><td>(<i>i</i>-C₅H₁₁)₃Si</td><td>TFA (6.7 eq)</td><td>62:38</td></tr><tr><td>(<i>c</i>-C₅H₉)₃Si</td><td>TFA (7 eq)</td><td>49:51</td></tr><tr><td>(<i>i</i>-Bu)₃Si</td><td>TFA (7 eq)</td><td>39:61</td></tr><tr><td>(<i>s</i>-Bu)₃Si</td><td>TFA (7 eq)</td><td>33:67</td></tr><tr><td>(<i>t</i>-Bu)₃Si</td><td>TFA (7.2 eq)</td><td>27:73</td></tr></table>	R_3Si	Acid Catalyst	I:II	<i>n</i> -BuH ₂ Si	BF ₃ •OEt ₂	76:24	Et ₂ HSi	BF ₃ •OEt ₂	52:48	Et ₃ Si	BF ₃ •OEt ₂	33:67	<i>n</i> -BuH ₂ Si	H ₂ SO ₄	81:19	Et ₂ HSi	H ₂ SO ₄	71:29	Et ₃ Si	H ₂ SO ₄	61:39	Et ₃ Si	TFA (6.8 eq)	58:42	(<i>n</i> -Bu) ₃ Si	H ₂ SO ₄	65:35	(<i>n</i> -C ₆ H ₁₃) ₃ Si	H ₂ SO ₄	68:32	(<i>i</i> -C ₅ H ₁₁) ₃ Si	TFA (6.7 eq)	62:38	(<i>c</i> -C ₅ H ₉) ₃ Si	TFA (7 eq)	49:51	(<i>i</i> -Bu) ₃ Si	TFA (7 eq)	39:61	(<i>s</i> -Bu) ₃ Si	TFA (7 eq)	33:67	(<i>t</i> -Bu) ₃ Si	TFA (7.2 eq)	27:73		
R_3Si	Acid Catalyst	I:II																																														
<i>n</i> -BuH ₂ Si	BF ₃ •OEt ₂	76:24																																														
Et ₂ HSi	BF ₃ •OEt ₂	52:48																																														
Et ₃ Si	BF ₃ •OEt ₂	33:67																																														
<i>n</i> -BuH ₂ Si	H ₂ SO ₄	81:19																																														
Et ₂ HSi	H ₂ SO ₄	71:29																																														
Et ₃ Si	H ₂ SO ₄	61:39																																														
Et ₃ Si	TFA (6.8 eq)	58:42																																														
(<i>n</i> -Bu) ₃ Si	H ₂ SO ₄	65:35																																														
(<i>n</i> -C ₆ H ₁₃) ₃ Si	H ₂ SO ₄	68:32																																														
(<i>i</i> -C ₅ H ₁₁) ₃ Si	TFA (6.7 eq)	62:38																																														
(<i>c</i> -C ₅ H ₉) ₃ Si	TFA (7 eq)	49:51																																														
(<i>i</i> -Bu) ₃ Si	TFA (7 eq)	39:61																																														
(<i>s</i> -Bu) ₃ Si	TFA (7 eq)	33:67																																														
(<i>t</i> -Bu) ₃ Si	TFA (7.2 eq)	27:73																																														
	Et ₃ SiH (1.1 eq), acid, rt	I + II (100)	74																																													
	<table><tr><th>Acid</th><th>I:II</th></tr><tr><td>BF₃•OEt₂</td><td>33:67</td></tr><tr><td>TFA</td><td>58:42</td></tr><tr><td>H₂SO₄</td><td>61:39</td></tr></table>	Acid	I:II	BF ₃ •OEt ₂	33:67	TFA	58:42	H ₂ SO ₄	61:39																																							
Acid	I:II																																															
BF ₃ •OEt ₂	33:67																																															
TFA	58:42																																															
H ₂ SO ₄	61:39																																															
	PhSiH ₃ (0.4 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE, O ₂ , rt	I + II (81), III 1:9	367																																													



R_3SiH (1.1 eq),
acid catalyst, 0° to rt, 24 h



381, 384




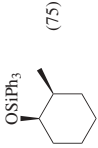
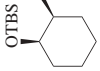
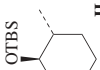
R_3Si	Acid Catalyst
$n-BuH_2Si$	$BF_3 \cdot OEt_2$ (1 eq)
Et_2HSi	$BF_3 \cdot OEt_2$ (1 eq)
Et_3Si	$BF_3 \cdot OEt_2$ (1 eq)
$n-BuH_2Si$	H_2SO_4 (1 eq)
Et_2HSi	H_2SO_4 (1 eq)
Et_3Si	H_2SO_4 (1 eq)
Et_3Si	TFA (6.8 eq)
$(n-Bu)_3Si$	H_2SO_4 (1 eq)
$n-PrH_2Si$	H_2SO_4 (1 eq)
$(n-C_6H_{13})_3Si$	TFA (1 eq)
$(i-C_3H_7)_3Si$	TFA (6.7 eq)
$(c-C_3H_9)_3Si$	TFA (7 eq)
$(i-Bu)_3Si$	TFA (7 eq)
$(s-Bu)_3Si$	TFA (2.3 eq)
$(s-Bu)_3Si$	TFA (7 eq)
$(i-Bu)_3Si$	TFA (7.2 eq)

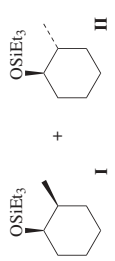
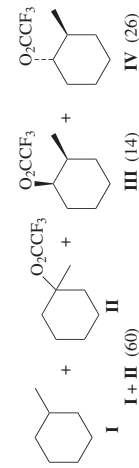
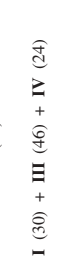
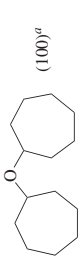
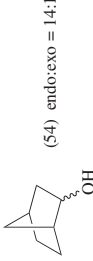


Silane, catalyst

Silane	Catalyst
PMHS	Triton-B
PMHS	TBAF
$(TMSO)_3SiH$	Triton-B
$(TMSO)_3SiH$	TBAF

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TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	R_3SiH (x eq), TBAF (5 eq), HMPA	 + 	320
	R_3Si x Temp Time	$I + II$ $I:II$	
	$PhMe_2Si$ 1.2 0° 24 h	(99) 76:24	
	Ph_2HSi 1.0 0° 5 h	(74) 86:14	
	Ph_2MeSi 1.2 0° 24 h	(81) 94:6	
	Ph_3Si 1.2 rt 12 h	(40) 95:5	
	Et_3SiH (1.1 eq), acid, rt	$I + II$ (100)	74
	Acid	$I:II$	
	$BF_3 \cdot OEt_2$	64:36	
	TFA	48:52	
	H_2SO_4	54:46	
	$PhSiH_3$ (0.4 eq), $Mn(dpm)_3$ (3 mol%), <i>i</i> -PrOH, DCE, O_2 , rt	$I + II$ (87), $I:II = 1:2.1$	367
	Et_3SiH (1 eq), $ZnCl_2$, reflux, 24 h	$I + II$ (50), $I:II = -$	382
	Ph_3SiH , $(C_6F_5)_3B$ (2 mol%), MeC_6H_5 , rt	 (75)	116
	TBBSH (3 eq), TBSOTf (0.01 eq), rt, 2 h	 +  $I + II$ (85), $I:II = 77:23$	392
	TBBSH (1.2 eq), $CuCl$ (0.5 mol%), NaOMe (3 mol%), 123 (0.1 mol%), Et_2O , rt, <3 h	$I + II$ (99), $I:II = 1.4:1$	749

Et ₃ SiH (5 eq), CuCl (3 mol%), NaOBu- <i>t</i> (3 mol%), <i>o</i> -dppb (0.05 mol%), MeC ₆ H ₅		749
(<i>t</i> -Bu) ₂ MeSiH (1 eq), TFA (6.6 eq), rt, 20 h		386
(<i>t</i> -Bu) ₂ SiH ₂ (1 eq), TFA (6.6 eq), rt, 20 h		386
Et ₃ SiH (2 eq), TMSOTf (0.1 eq), CH ₂ Cl ₂ , rt, 2 h		334
PhSiH ₃ (0.4 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE, O ₂ , rt		367
Et ₃ SiH (5 eq), CuCl (3 mol%), NaOBu- <i>t</i> (20 mol%), 210 (3 mol%), MeC ₆ H ₅ , rt		412
Et ₃ SiH (1.1 eq), H ₂ SO ₄ , H ₂ O, MeCN, 28°, 65 h		313

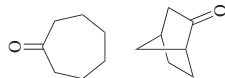
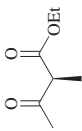
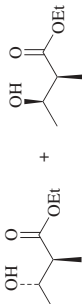
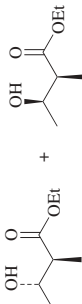
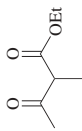


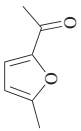

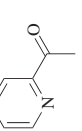

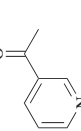

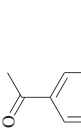

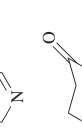




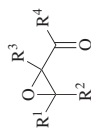


TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMe ₂ SiH (1.2 eq), TFA, 0°, 10 h	 +  I + II (90), I:II = 1:1	87, 276
	TMSH (1.1 eq), TMSI (5 mol%), <i>n</i> -C ₃ H ₇ OTMS (1 eq), CH ₂ Cl ₂ , 0-15°, rt, 2 h	 I +  II (90)	334
	PhMe ₂ SiH (1.1 eq), CsF (5 mol%), 18-C-6 (2.5 mol%), CH ₂ Cl ₂ , rt, 1 h	 (85)	346
	PhMe ₂ SiH (1.1 eq), CsF (10 mol%), 18-C-6 (0.5 mol%), CH ₂ Cl ₂ , rt, 5.5 h	 (67)	345
	PhMe ₂ SiH (1.1 eq), CsF (10 mol%), 18-C-6 (0.5 mol%), CH ₂ Cl ₂ , rt, 15 h	 (60)	345
	PhMe ₂ SiH (1.1 eq), CsF (10 mol%), 18-C-6 (0.5 mol%), CH ₂ Cl ₂ , rt, 3 h	 (71)	345
	Et ₃ SiH (0.8 eq), TFA (6.5 eq), rt, 24 h	 I +  II +  III +  IV	72

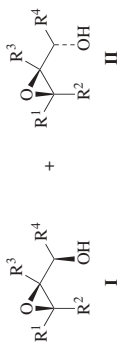


(MeO)₃SiH (1.2 eq),
LiOMe (0.04 eq), solvent

R ¹	R ²	R ³	R ⁴
H	H	H	<i>n</i> -Bu
H	H	H	<i>n</i> -Bu
H	H	Me	<i>n</i> -Bu
H	H	Me	<i>n</i> -Bu
H	H	H	Ph
H	H	H	Ph
H	H	Me	Ph
H	H	Me	Ph
Me	H	H	Ph
Me	H	H	Ph
Me	Me	H	Ph
Me	Me	H	Ph

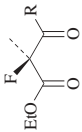
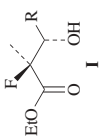
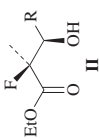
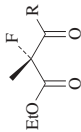
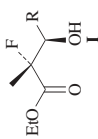
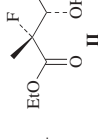


Solvent	Temp	Time
Et ₂ O	-20°	2 h
HMPA	0°	23 h
Et ₂ O	-20°	2 h
HMPA	0°	23 h
Et ₂ O	-20°	9 h
HMPA	0°	22 h
Et ₂ O	-20°	18 h
HMPA	0°	22 h
Et ₂ O	-20°	6 h
HMPA	0°	22 h
Et ₂ O	-20°	2 h
HMPA	0°	22 h

R	I + II	I:II	III + IV	III:IV
4-Me	(83)	0.56	(17)	—
3-Me	(87)	0.72	(13)	—
2-Me	(>99)	0.92	(<1)	—
3,3,5-Me ₃	(84)	8.1	(16)	3.65
4- <i>t</i> -Bu	(83)	0.47	(17)	1.04



I + II	I:II
(78)	11:89
(80)	81:19
(84)	11:89
(90)	44:56
(100)	8:92
(98)	90:10
(91)	34:66
(91)	72:28
(99)	9:91
(100)	93:7
(88)	0:100
(100)	60:40

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.														
	PhMe ₂ SiH (1.25 eq), AlCl ₃ , CH ₂ Cl ₂ , rt	 I +  II <table><tr><th>I + II</th><th>I:II</th></tr><tr><td>(45)</td><td>98:2</td></tr><tr><td>(65)</td><td>96:4</td></tr><tr><td>(74)</td><td>99:1</td></tr><tr><td>(45)</td><td>98:2</td></tr><tr><td>(71)</td><td>97:3</td></tr><tr><td>(65)</td><td>99:1</td></tr></table>	I + II	I:II	(45)	98:2	(65)	96:4	(74)	99:1	(45)	98:2	(71)	97:3	(65)	99:1	90
I + II	I:II																
(45)	98:2																
(65)	96:4																
(74)	99:1																
(45)	98:2																
(71)	97:3																
(65)	99:1																
	PhMe ₂ SiH (1.25 eq), TBAF (0.05 eq), DMF	 I +  II <table><tr><th>I + II</th><th>I:II</th></tr><tr><td>(51)</td><td>21:79</td></tr><tr><td>(67)</td><td>14:86</td></tr><tr><td>(74)</td><td>17:83</td></tr><tr><td>(49)</td><td>4:96</td></tr></table>	I + II	I:II	(51)	21:79	(67)	14:86	(74)	17:83	(49)	4:96	90				
I + II	I:II																
(51)	21:79																
(67)	14:86																
(74)	17:83																
(49)	4:96																
	R ₃ SiH (1 eq), Et ₂ O, ZnCl ₂ , 35°		383														

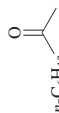
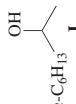

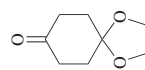
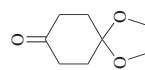



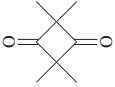
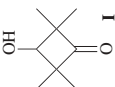
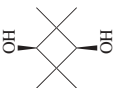

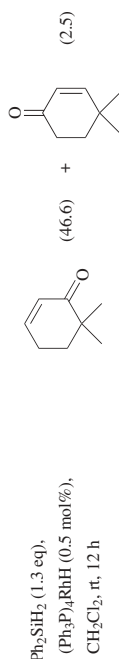
R ¹	R ²	R ₃ Si	Time		
—(CH ₂) ₅ —		(<i>n</i> -Bu) ₃ Si	2 h	(25)	
—(CH ₂) ₅ —		Et ₃ Si	2 h	(26)	
<i>n</i> -Pr	<i>n</i> -Pr	(<i>n</i> -Bu) ₃ Si	3 h	(31)	
Et	<i>n</i> -Bu	(<i>n</i> -Bu) ₃ Si	3 h	(34)	
<i>n</i> -Bu	<i>n</i> -Pr	Et ₃ Si	2 h	(79)	
<i>n</i> -Bu	<i>n</i> -Bu	Et ₃ Si	3 h	(57)	
Me	<i>n</i> -C ₇ H ₁₅	Et ₃ Si	4 h	(22)	
Et	Bn	Et ₃ Si	3 h	(29)	
<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₅ H ₁₁	Et ₃ Si	5 h	(59)	
<i>n</i> -C ₈ H ₁₇	<i>n</i> -C ₈ H ₁₇	Et ₃ Si	4 h	(35)	
C ₈		PhMe ₂ SiH (1.2 eq), [Rh(C ₂ H ₄) ₂] ₂ (0.5 mol%), P(tm-tp) ₃ (2 mol%), C ₆ H ₆ , rt, 6 h PhMe ₂ SiH (1.2 eq), [Rh(C ₂ H ₄) ₂] ₂ (0.5 mol%), P(tp) ₃ (2 mol%), C ₆ H ₆ , rt, 6 h PhMe ₂ SiH (1.2 eq), [Rh(C ₂ H ₄) ₂] ₂ (0.5 mol%), PPh ₃ (2 mol%), C ₆ H ₆ , rt, 6 h TMSH (4 eq), TMSOTf (1.6 mol%), CH ₂ Cl ₂ , 0°, 4 h; rt, 2 h PhSiH ₃ (0.4 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE, O ₂ , rt	 (91)	389	
				I (41)	389
				I (31)	389
				 (92)	392
				(—)	367

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

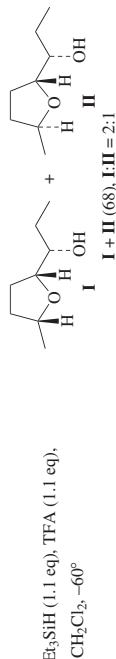
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	PMHS (2.5 eq), (Ph ₃ P)CuH (3 mol%), MeC ₆ H ₅ , 10 h	 I (80) (97)	317
	Me(EtO) ₂ SiH (1.5 eq), KF (1 eq), DMF, 80°, 3 h	I (80)	82
	Et ₃ SiH (1 eq), ZnCl ₂ , 105°, 16 h	 I (70)	382
	R ₃ SiH (2 eq), (Ph ₃ P) ₃ RhCl, C ₆ H ₆ , rt,	  I  II  III	370
<div style="display: flex; justify-content: space-around;"> <div> % Conversion I </div> <div> II + III </div> <div> II:III </div> </div>			
R ₃ Si	Time		
<i>n</i> -C ₅ H ₁₁ H ₂ Si	2 h	100 (0)	52-48
<i>n</i> -BuMeHSi	2 h	35 (100)	(0) —
(<i>n</i> -Pr) ₂ HSi	1 h	60 (100)	(0) —
(<i>n</i> -Pr) ₂ HSi	5 h	100 (100)	(0) —
Ph ₂ HSi	2 h	100 (5)	(95) 65:35
Ph ₂ HSi (1 eq)	2 h	51 (—)	(0) —
Et ₃ Si	24 h	0 (—)	(—) —
Et ₃ Si (60°)	24 h	0 (100)	(—) —
Et ₂ MeSi	24 h	100 (100)	(0) —
Et ₂ MeSi, then Ph ₂ HSi	24 h, +3 h	100 (35)	(65) 46:54

R_3SiH , $[Rh(cod)Cl]_2$,
ligand, C_6H_6 , rt, 2 h

R_3Si	Ligand	I	II + III	II:III
Ph_2HSi	PPh_3	(—)	(100)	63:37
$n-C_5H_{11}H_2Si$	PPh_3	(—)	(100)	53:47
Ph_2HSi	diphenylenephosphine	(—)	(100)	57:43
$n-C_5H_{11}H_2Si$	diphenylenephosphine	(—)	(100)	55:45
Ph_2HSi	dppe	(80)	(20)	69:31



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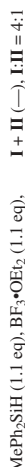
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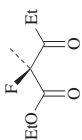
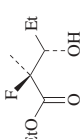
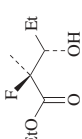
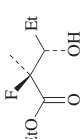
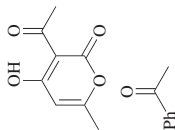
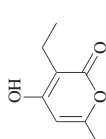









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




TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

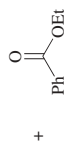
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
 C ₈	PhMe ₂ SiH (1.25 eq), catalyst (x eq), CH ₂ Cl ₂ , rt	 I	90																																								
	<table><tr><th>Catalyst</th><th>x</th><th>Time</th><th>I + II</th><th>I:II</th></tr><tr><td>AlCl₃</td><td>1.5</td><td>2 h</td><td>(65)</td><td>96:4</td></tr><tr><td>AlCl₃</td><td>1.5</td><td>3 h</td><td>(80)</td><td>96:4</td></tr><tr><td>AlCl₃</td><td>1.5</td><td>4 h</td><td>(73)</td><td>98:2</td></tr><tr><td>AlCl₃</td><td>1.0</td><td>4 h</td><td>(51)</td><td>98:2</td></tr><tr><td>EtCl₂Al</td><td>1.5</td><td>3 h</td><td>(61)</td><td>97:3</td></tr><tr><td>EtCl₂Al</td><td>1.1</td><td>4 h</td><td>(54)</td><td>98:2</td></tr><tr><td>EtCl₂Al</td><td>1.1</td><td>10 h</td><td>(68)</td><td>94:6</td></tr></table>	Catalyst	x	Time	I + II	I:II	AlCl ₃	1.5	2 h	(65)	96:4	AlCl ₃	1.5	3 h	(80)	96:4	AlCl ₃	1.5	4 h	(73)	98:2	AlCl ₃	1.0	4 h	(51)	98:2	EtCl ₂ Al	1.5	3 h	(61)	97:3	EtCl ₂ Al	1.1	4 h	(54)	98:2	EtCl ₂ Al	1.1	10 h	(68)	94:6	 I	 I:II
Catalyst	x	Time	I + II	I:II																																							
AlCl ₃	1.5	2 h	(65)	96:4																																							
AlCl ₃	1.5	3 h	(80)	96:4																																							
AlCl ₃	1.5	4 h	(73)	98:2																																							
AlCl ₃	1.0	4 h	(51)	98:2																																							
EtCl ₂ Al	1.5	3 h	(61)	97:3																																							
EtCl ₂ Al	1.1	4 h	(54)	98:2																																							
EtCl ₂ Al	1.1	10 h	(68)	94:6																																							
 C ₈	Et ₃ SiH, TFA, LiClO ₄ (0.01 eq), rt, 4 h	 (85)	423																																								
	Et ₃ SiH (2.5 eq), TFA (5 eq), 20°	 I	180																																								
	Et ₃ SiO(EtHSiO) ₃ SiEt ₃ (0.5 mol%), TFA (9 eq), CHCl ₃ , 50°, 15 h	 I (94)	207																																								
	Et ₃ SiH (2 mol%), TFA (9 eq), CHCl ₃ , 50°, 3 h	 I (100)	207																																								
	Et ₃ SiH (3 eq), TFA (5 eq), 50°, 15 h	 I (80)	210																																								
	Et ₃ SiH (3 eq), BF ₃ •OEt ₂ (14.6 mol%), 50°, 1 h	 I (80)	210																																								
	Et ₃ SiH (1.1-1.2 eq), HCO ₂ H, HOAc, KU-1, 55°, 5 h	 I (81)	208																																								

Et ₃ SiH (1.2 eq), 65% HClO ₄ , CH ₂ Cl ₂ , 20°, 30 min	I (74)	214
Et ₃ SiH (2.5 eq), AlCl ₃ (0.5 eq), HCl, CH ₂ Cl ₂ , rt, 15 min	I (95)	136
Et ₃ SiH (1.5 eq), CF ₃ SO ₃ H (4 eq), CH ₂ Cl ₂ , 0° to rt, 2 h	I (80) ^b	420
Cl ₃ SiH (1.5 eq), CH ₂ Cl ₂ /DMF (4:1), 0°, 12 h	 II	318 (54)
(MeO) ₃ SiH (1.5 eq), LiOCMe ₂ Me ₂ OLi (0.08 eq), THF, 0°	II (98)	92
PMHS (200 mol%), Sn(OTf) ₂ (10 mol%), TMEDA (10 mol%), MeOH, rt	II (98)	385
(EtO) ₂ MeSiH (2.3 eq), CsF (1 eq), 100°, 2.5 h	II (70)	83
(EtO) ₃ SiH (2.3 eq), CsF (1 eq), 0°, 0.5 h	II (80)	83
PMHS (2.3 eq), KF (1 eq), DMF, 0°, 0.5 h	II (80)	83
Me(EtO) ₂ SiH (1.5 eq), KF (1 eq), DMF, 80°, 1.5 h	II (78)	82
PMHS (1.5 eq), KF (1 eq), DMF, 30°, 2.5 h	II (78)	82, 83
R ₃ SiH (1 eq), MF	II	80, 83

R ₃ Si	MF	Temp	Time
Me(EtO) ₂ Si	CsF	100°	2.5 h
Me(EtO) ₂ Si	KF	100°	24 h
(EtO) ₃ Si	KF	100°	1 h
(EtO) ₃ Si	CsF	0°	0.5 h

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	PMHS (1 eq), ZnCl_2 (1 eq), Et_2O , rt, 24 h	 II (52)	315
	D , 0° , 12 h	II (50)	93
	E , rt, 12 h	II (50)	93
	H , rt, 12 h	II (97)	93
	G , 0° , 2 h	II (98)	93
	L , THF, 0° , 2 h	II (88)	96
	PhSiH_3 (0.4 eq), $\text{Mn}(\text{dpm})_3$ (3 mol%), <i>i</i> -PrOH, DCE, O_2 , rt	II (24)	367
	Et_3SiH (1.2 eq), 208 (0.2 mol%), rt, 23 h	I (2) + II (89)	377
 +	PMHS (1.2 eq), KF (1.3 eq), DMSO, 40° , 4 h	II (85) +  III (0)	82, 83
 +	$(\text{EtO})_3\text{SiH}$ (2.3 eq), CsF (1 eq), rt, 1 min	II (100) + III (0)	83












+



+

Activator	x	Time	II (100) + III (0)	83
Me(EtO) ₂ SiH (2.3 eq), CsF (1 eq), DMF, 40°, 4 h	1.5	12 h	II (>99) + III (<1)	116
Ph ₃ SiH (1 eq), (C ₆ F ₅) ₃ B (2 mol%), MeC ₆ H ₅ , rt	0.1	24 h		379
Cl ₃ SiH (1.5 eq), activator (x eq), CH ₂ Cl ₂ , 0° to rt	1.5	12 h		
	1.5	12 h		
	1.5	12 h		
	1.5	12 h		
	1.5	12 h		
	0.1	24 h		
	1.5	12 h		
	1.5	12 h		
	1.5	12 h		
Et ₃ SiH (2 eq), TMSOTf (0.1 eq), CH ₂ Cl ₂ , rt, 2 h	1.5	12 h	II (minor) + (major)	334

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.	
	1. HC(OMe) ₃ , CH ₂ Cl ₂ , rt, 2 h 2. Et ₃ SiH, Nafion [®] -H, CH ₂ Cl ₂ , reflux, 3 h	 (91)	335	
	Et ₃ SiH (1 eq), TMSOTf (0.1 eq), ROTMS (0.83 eq), CH ₂ Cl ₂	 OR 	R Temp allyl -30° to 0° (85) Bn -78° to -30° (100) <i>c</i> -C ₆ H ₁₁ 0° to rt (96) <i>t</i> -Bu 0° to rt (28)	341
	Et ₃ SiH (1 eq), ZnCl ₂ , 95°, 150 h	 (40) I		382
	Et ₃ SiH, 227 or 228 or 229 (5 mol%)	I (100)		117
	Ph ₂ SiH ₂ (1 eq), [Cp [*] (Me ₃ P)Ir(η ₁₂ -SiPh ₂ C ₆ H ₄)(H))] ⁺ [[C ₆ F ₅) ₄ B] ⁻ (5 mol%), CD ₂ Cl ₂ , rt, 18h	 (20) +  (54)	OSiPh ₂ H	745
Ph(Np-1)SiH ₂ , (Ph ₃ P) ₃ RbCl (5 x 10 ⁻⁴ M)		 OSiHPh ₂ (Np-1) (80) +  (20)		744

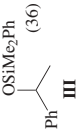

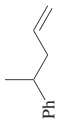

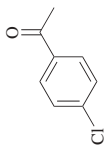
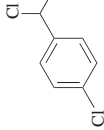
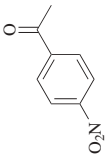
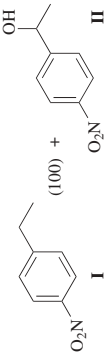

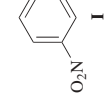
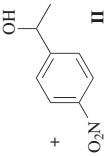
PhMe ₂ SiH (1.2 eq), TBAF (2 eq), HMPA, rt, 0.5 h	II (40) + 	320																																				
PhMe ₂ SiH (1.1 eq), CsF (0.1 eq), 18-C-6 (0.05 eq), CH ₂ Cl ₂ , rt, 7 h	III (54)	346, 347																																				
PhMe ₂ SiH (1.1 eq), catalyst (0.1 eq), 18-C-6 (0.05 eq), solvent, rt	III	346, 347																																				
	<table> <tr> <th>Catalyst</th><th>Solvent</th><th>Time</th></tr> <tr> <td>CsF</td><td>CH₂Cl₂</td><td>5 h</td></tr> <tr> <td>CsF</td><td>THF</td><td>14 h</td></tr> <tr> <td>CsF</td><td>C₆H₆</td><td>29 h</td></tr> <tr> <td>RbF</td><td>THF</td><td>21 h</td></tr> <tr> <td>RbF</td><td>CH₂Cl₂</td><td>21 h</td></tr> <tr> <td>KF</td><td>CH₂Cl₂</td><td>75 h</td></tr> <tr> <td>KF</td><td>THF</td><td>25 h</td></tr> <tr> <td>KF</td><td>C₆H₆</td><td>35 h</td></tr> <tr> <td>NaF</td><td>THF</td><td>19 h</td></tr> <tr> <td>LiF</td><td>THF</td><td>75 h</td></tr> <tr> <td>KF-Al₂O₃</td><td>THF</td><td>24 h</td></tr> </table>	Catalyst	Solvent	Time	CsF	CH ₂ Cl ₂	5 h	CsF	THF	14 h	CsF	C ₆ H ₆	29 h	RbF	THF	21 h	RbF	CH ₂ Cl ₂	21 h	KF	CH ₂ Cl ₂	75 h	KF	THF	25 h	KF	C ₆ H ₆	35 h	NaF	THF	19 h	LiF	THF	75 h	KF-Al ₂ O ₃	THF	24 h	(100) (100) (92) (76) (100) (52) (46) (73) (0) (0) (1)
Catalyst	Solvent	Time																																				
CsF	CH ₂ Cl ₂	5 h																																				
CsF	THF	14 h																																				
CsF	C ₆ H ₆	29 h																																				
RbF	THF	21 h																																				
RbF	CH ₂ Cl ₂	21 h																																				
KF	CH ₂ Cl ₂	75 h																																				
KF	THF	25 h																																				
KF	C ₆ H ₆	35 h																																				
NaF	THF	19 h																																				
LiF	THF	75 h																																				
KF-Al ₂ O ₃	THF	24 h																																				

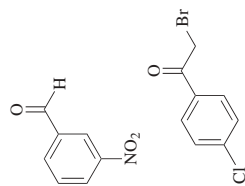
TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₈	Me ₂ ClSiH, TMSCH ₂ CH=CH ₂ , catalyst (5 mol%), solvent, rt, 2 h Catalyst Solvent		427
	InCl ₃ CH ₂ Cl ₂	(86)	
	InBr ₃ CH ₂ Cl ₂	(60)	
	InI ₃ CH ₂ Cl ₂	(85)	
	AlCl ₃ CH ₂ Cl ₂	(1)	
	Se(OTf) ₃ CH ₂ Cl ₂	(<0.2)	
	InCl ₃ ClCH ₂ CH ₂ Cl	(63)	
	InCl ₃ C ₆ H ₁₂	(0)	
	InCl ₃ DMF	(0)	
	InCl ₃ THF	(0)	
	InCl ₃ MeCN	(35)	
	InCl ₃ CHCl ₃	(16)	
	InCl ₃ CCl ₄	(0)	
	Me ₂ ClSiH (1.2 eq), In(OH) ₃ (5 mol%), CHCl ₃ , rt, 0.5 h	 (78)	331
	Me ₂ ClSiH (1.2 eq), In(OH) ₃ (5 mol%), CHCl ₃ , rt, 0.5 h	 (76)	331
	1. Et ₃ SiH, BF ₃ , CH ₂ Cl ₂ 2. BF ₃ •OEt ₂ , rt, 30 min	 (100) +  (0)	I
	1. Et ₃ SiH, BF ₃ , CH ₂ Cl ₂ 2. BF ₃ •OEt ₂ , rt, 3 min	 I (0) + II (100)  II	I

ClMe₂SiH (1.2 eq), catalyst (5 mol%),
CHCl₃, rt, 2 h

Catalyst
none
In(OH) ₃
Sc(OTf) ₃
TiCl ₄
(C ₆ F ₅) ₃ B

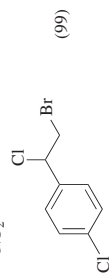
I	II
(0)	(0)
(0)	(99)
(0)	(69)
(7)	(0)
(81)	(0)



(80)

80

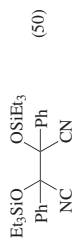
Me₂ClSiH (1.2 eq),
In(OH)₃ (5 mol%), CHCl₃, rt, 4 h



(99)

331

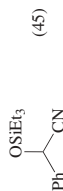
Et₃SiH (1 eq), (Ph₃P)₃RhCl



(50)

411

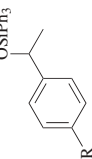
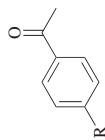
Et₃SiH (1 eq), PdCl₂



(45)

411






Ph₃SiH (1 eq), (C₆F₅)₃B (2 mol%)



R	R
H	(76)
Me	(84)
Cl	(80)
NO ₂	(91)

115

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 	Ph_3SiH , $(C_6F_5)_3B$ (2 mol%), MeC_6H_5 , rt	Ar	
		Ph	(76)
		4-MeC ₆ H ₄	(84)
		4-ClC ₆ H ₄	(80)
		4-O ₂ NC ₆ H ₄	(91)
C_{8-10} 	$HMe_2SiOSiMe_2H$ (1.0 eq), I_2 (0.6 eq), CH_2Cl_2 , -5°	Ar	
		Ph	5 min (76)
		4-MeC ₆ H ₄	20 min (65)
		R ¹	
		R ²	
C_{8-11} 	Et_3SiH (1 eq), R ² OTMS (1 eq), $TrClO_4$ (5 mol%), CH_2Cl_2 , 0°, 5 min	Ph	BnCH ₂ CH ₂ (69)
		Ph	Bn (76)
		BnCH ₂	BnCH ₂ CH ₂ (68)
		Ar	
		Ph	(93)
C_{8-11} 	$PMHS$ (3 eq), TBAF (2 mol%), THF , rt	Ph	(93)
		4-FC ₆ H ₄	(86)
		4-ClC ₆ H ₄	(96)
		4-O ₂ NC ₆ H ₄	(92)
		3,4-[OCH ₂ O]C ₆ H ₃	(93)
C_{8-11} 	$PMHS$ (3 eq), Triton-B (2 mol%), THF , rt	Ar	
		4-FC ₆ H ₄	(97)
		4-ClC ₆ H ₄	(88)
		4-MeC ₆ H ₄	(88)
		3,4,5-(MeO) ₃ C ₆ H ₂	(93)

C₈,12(EtO)₃SiH, **194** (10 mol%), Et₂O

378

R	Temp	Time
<i>n</i> -C ₆ H ₁₃	40°	12 h
<i>c</i> -C ₆ H ₁₁	40°	12 h
<i>n</i> -C ₄ H ₉ C≡C	40°	12 h
(<i>E</i>)- <i>n</i> -C ₅ H ₁₁ CH=CH	40°	12 h
1-C ₁₀ H ₇	50°	5 h
Ph	50°	5 h
4-MeOC ₆ H ₄	50°	5 h
4-ClC ₆ H ₄	50°	5 h
4-O ₂ NC ₆ H ₄	50°	5 h
3-O ₂ NC ₆ H ₄	50°	5 h

(84)
(77)
(50)
(>98)
(>98)
(>98)
(>98)
(>98)
(>98)
(>98)

C₈,13[H₂Si(OSiPr-*t*)₃]K (x eq), rt, 4 h

750

R	x
Me	(36) 0.5
Me	(80) 1.0
Ph	(50) 0.5

[HSi(OEt)₄]K, THF, rt**I**

R	Time
Me	15 h (53)
Ph	4 h (73)









288

Ph₂SiH₂ (1 eq), KF, 100°

78

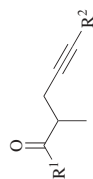
R ¹	R ²
—(CH ₂) ₅ —	(70)
Ph	Me (40)
Ph	Ph (30)

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																
<div>C₈,13</div> <div></div>	<div></div> <div>Me₂ClSiH, TMSCH₂CH=CH₂, InCl₃ (5 mol%), CH₂Cl₂, rt</div>	<div></div>	427																
<div><table><tr><th>Ar</th><th>R</th></tr><tr><td><i>p</i>-ClC₆H₄</td><td>Me</td></tr><tr><td>Ph</td><td>Et</td></tr><tr><td>Ph</td><td>ClCH₂CH₂</td></tr><tr><td>PhCH₂CH₂</td><td>Me</td></tr><tr><td><i>p</i>-EtO₂CC₆H₄</td><td>Me</td></tr><tr><td>Ph</td><td>Ph</td></tr><tr><td><i>p</i>-NO₂C₆H₄</td><td>Ph</td></tr></table></div>	Ar	R	<i>p</i> -ClC ₆ H ₄	Me	Ph	Et	Ph	ClCH ₂ CH ₂	PhCH ₂ CH ₂	Me	<i>p</i> -EtO ₂ CC ₆ H ₄	Me	Ph	Ph	<i>p</i> -NO ₂ C ₆ H ₄	Ph	<div>2 h (84) 2 h (67) 1 h; 60°, 3 h (70) 2 h mixture 1 h; 60°, 3 h (44) 2 h (99) 1 h; 60°, 2 h (75)</div>		
Ar	R																		
<i>p</i> -ClC ₆ H ₄	Me																		
Ph	Et																		
Ph	ClCH ₂ CH ₂																		
PhCH ₂ CH ₂	Me																		
<i>p</i> -EtO ₂ CC ₆ H ₄	Me																		
Ph	Ph																		
<i>p</i> -NO ₂ C ₆ H ₄	Ph																		
<div>C₈,17</div> <div></div>	<div></div> <div>Et₃SiH (1.1 eq), H₂SO₄, H₂O, MeCN, 28°</div>	<div></div> <table><tr><th>R¹</th><th>R²</th><th>Time</th></tr><tr><td>—(CH₂)₅—</td><td></td><td>72 h (30)</td></tr><tr><td>Ph</td><td>Me</td><td>72 h (85)</td></tr><tr><td>Ph</td><td>Ph</td><td>48 h (63)</td></tr></table>	R ¹	R ²	Time	—(CH ₂) ₅ —		72 h (30)	Ph	Me	72 h (85)	Ph	Ph	48 h (63)	313				
R ¹	R ²	Time																	
—(CH ₂) ₅ —		72 h (30)																	
Ph	Me	72 h (85)																	
Ph	Ph	48 h (63)																	
<div>C₈,17</div> <div></div>	<div></div> <div>Et₃SiH (x eq), TFA (y eq), solvent, rt</div>		73																

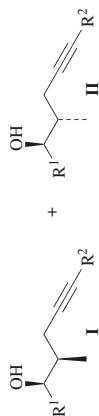
Ar	R	x	y	Solvent	Time
Ph	Me	2.2	10.0	TFA	15 min
4-ClC ₆ H ₄	Me	2.2	6.7	TFA	200 h
Ph	BrCH ₂	4.4	7.0	TFA	44 h
Ph	Et	2.5	5.4	TFA	15 min
Ph	<i>n</i> -Pr	2.2	10.0	TFA	15 min
Ph	<i>i</i> -Pr	2.5	5.4	TFA	15 min
Ph	<i>c</i> -C ₃ H ₅	2.6	9.5	H ₂ O-TFA	7 h
Ph	<i>n</i> -Bu	2.2	10.0	TFA	15 min
Ph	HO ₂ C(CH ₂) ₃	2.2	6.5	TFA	48 h
Ph	<i>c</i> -C ₄ H ₇	2.2	9.9	H ₂ O-TFA	6 h
Ph	<i>c</i> -C ₄ H ₇	5.0	5.0	CCl ₄ -TFA	7.5 h
Ph	HO ₂ C(CH ₂) ₄	2.4	7.0	TFA	5.5 h
Ph	Ph	2.2	15.0	TFA	15 min
4-O ₂ NC ₆ H ₄	Ph	2.4	7.7	TFA	47 h
4-HO ₂ CC ₆ H ₄	Ph	3.0	6.7	CCl ₄ -TFA	120 h
Ph	<i>n</i> -C ₁₀ H ₂₁	2.2	10.0	TFA	15 min

C₈₋₁₈



Et₃SiH, (C₆F₅)₃B (2 mol%),
MeC₆H₅, 0°, 1 h

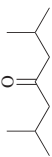
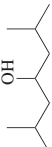
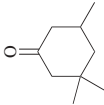
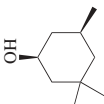
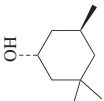
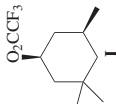
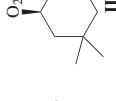
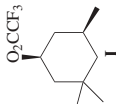
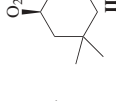
R ¹	R ²
Et	H
<i>t</i> -Bu	H
<i>c</i> -C ₆ H ₁₁	H
Ph	H
Ph	Me
Ph	Ph
Ph	TMS
2-MeC ₆ H ₄	H



I + II	I:II
(100)	4.4:1
(100)	>30:1
(93)	5.0:1
(90)	7.0:1
(100)	5.0:1
(100)	3.0:1
(100)	7.7:1
(94)	15:1

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TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																			
 C ₉	(EtO) ₃ SiH (1 eq), CsF, rt, 1 h	 I (95)	80																																			
	Me(EtO) ₂ SiH (1.5 eq), KF (1 eq), DMF, 60°, 5.5 h	I (75)	82																																			
	PMHS (1.5 eq), KF•2H ₂ O (1 eq), DMSO, 60°, 7 h	I (85)	82																																			
	1. R ₃ SiH (1.1 eq), acid catalyst (1 eq), 0° to rt, 24 h 2. Aq. OH ⁻	 I +  II I + II (—)	381, 384																																			
	<table><tr><th>R₃Si</th><th>Acid Catalyst</th><th>I:II</th></tr><tr><td><i>n</i>-BuH₂Si</td><td>BF₃•OEt₂</td><td>13:87</td></tr><tr><td>Et₂HSi</td><td>BF₃•OEt₂</td><td>9:91</td></tr><tr><td>Et₃Si</td><td>BF₃•OEt₂</td><td>5:95</td></tr><tr><td>Et₃Si</td><td>TFA (6.8 eq)</td><td>16:84</td></tr><tr><td><i>n</i>-BuH₂Si</td><td>H₂SO₄</td><td>26:74</td></tr><tr><td>Et₂HSi</td><td>H₂SO₄</td><td>15:85</td></tr><tr><td>Et₃Si</td><td>H₂SO₄</td><td>10:90</td></tr><tr><td>(<i>n</i>-Bu)₃Si</td><td>H₂SO₄</td><td>11:89</td></tr></table>	R ₃ Si	Acid Catalyst	I:II	<i>n</i> -BuH ₂ Si	BF ₃ •OEt ₂	13:87	Et ₂ HSi	BF ₃ •OEt ₂	9:91	Et ₃ Si	BF ₃ •OEt ₂	5:95	Et ₃ Si	TFA (6.8 eq)	16:84	<i>n</i> -BuH ₂ Si	H ₂ SO ₄	26:74	Et ₂ HSi	H ₂ SO ₄	15:85	Et ₃ Si	H ₂ SO ₄	10:90	(<i>n</i> -Bu) ₃ Si	H ₂ SO ₄	11:89	<table><tr><th>Acid</th><th>I:II</th></tr><tr><td>BF₃•OEt₂</td><td>95:5</td></tr><tr><td>TFA</td><td>84:16</td></tr><tr><td>H₂SO₄</td><td>90:10</td></tr></table>	Acid	I:II	BF ₃ •OEt ₂	95:5	TFA	84:16	H ₂ SO ₄	90:10	74
R ₃ Si	Acid Catalyst	I:II																																				
<i>n</i> -BuH ₂ Si	BF ₃ •OEt ₂	13:87																																				
Et ₂ HSi	BF ₃ •OEt ₂	9:91																																				
Et ₃ Si	BF ₃ •OEt ₂	5:95																																				
Et ₃ Si	TFA (6.8 eq)	16:84																																				
<i>n</i> -BuH ₂ Si	H ₂ SO ₄	26:74																																				
Et ₂ HSi	H ₂ SO ₄	15:85																																				
Et ₃ Si	H ₂ SO ₄	10:90																																				
(<i>n</i> -Bu) ₃ Si	H ₂ SO ₄	11:89																																				
Acid	I:II																																					
BF ₃ •OEt ₂	95:5																																					
TFA	84:16																																					
H ₂ SO ₄	90:10																																					
	Et ₃ SiH (1.1 eq), acid, rt	 I +  II I + II (100)	74																																			
	(<i>n</i> -Bu) ₂ SiH ₂ (1 eq), TFA (6.6 eq), rt, 20 h	 I +  II I + II (89)	386																																			

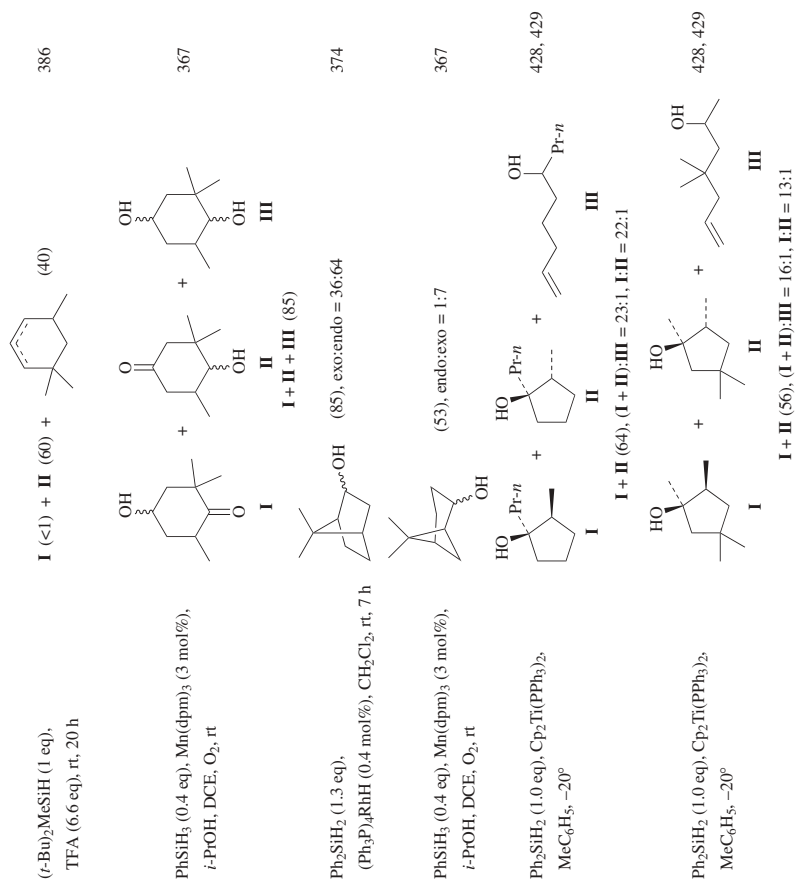
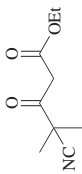
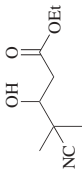
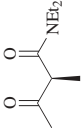
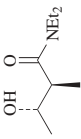
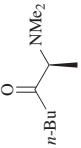
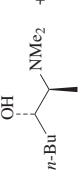
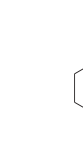
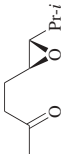
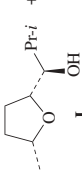

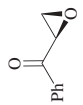
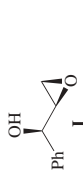








TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph_3SiH_2 (1.2 eq), AlCl_3 (1 eq), CH_2Cl_2 , 20° , 19 h	 (90) + Ph_2SiHCl (—)	373
	PhMe_2SiH (1.2 eq), TFA, 0° , 3 h	 I + II (94), I:II = 2:98	87, 276
	PhMe_2SiH (1.1-1.2 eq), TBAF (5-10 mol%), HMPA, rt, 10 h	 I + II (83), I:II >99:1	320
	Ph_3SiH_2 (1.1-1.2 eq), TBAF (5-10 mol%), HMPA, rt, 12 h	I + II (97), I:II = 98:2	320
	Ph_3SiH (4 eq), catalyst (2.2 eq), CH_2Cl_2 , -78° , 6 h; 0° , 12 h	 I + II (83), I:II >99:1	407
	Catalyst $\text{BF}_3 \cdot \text{OEt}_2$ TMSOTf	I + II + III I:II:III (67) 6:1:2 (81) 20:1:1.3	366
	$(\text{MeO})_3\text{SiH}$ (1.2 eq), LiOMe (0.04 eq), Et_2O , -20° , 1 d	 I + II (97), I:II = 6:94	366
	$(\text{MeO})_3\text{SiH}$ (1.2 eq), LiOMe (1.2 eq), Et_2O , -20° , 1 d	I + II (19), I:II = 68:32	366

	<p>I + II (96), II = 4:96</p>	366
<p>OLi (1.2 eq), (MeO)₃SiH (1.2 eq), Et₂O, -20°, 1 d</p>		
<p>Et₃SiH (1.2 eq), 123 (0.05 mol%), CuCl (0.5 mol%), NaOBu-<i>t</i> (0.1 mol%), Et₂O, 4 h</p>	<p>Et₃SiO  I (95)</p>	749
<p>Et₃SiH (1.2 eq), CuCl (0.5 mol%), NaOBu-<i>t</i> (0.1 mol%), <i>o</i>-dppb (0.05 mol%), neat, microwave, 15 min</p>	<p>I (98)</p>	749
<p><i>t</i>-BuMe₂SiH (1.2 eq), CuCl (0.5 mol%), NaOMe (3 mol%), 123 (0.05 mol%), MeC₆H₅, Et₂O, or CH₂Cl₂, rt, <3 h</p>	<p><i>t</i>-BuMe₂SiO  I (100)</p>	749
<p><i>t</i>-BuMe₂SiH (1.2 eq), CuCl (0.5 mol%), NaOMe (3 mol%), <i>o</i>-dppb (0.05 mol%), MeC₆H₅, rt, <5 h</p>	<p>I (99)</p>	749
<p><i>t</i>-BuMe₂SiH (1.2 eq), CuCl (0.5 mol%), NaOMe (3 mol%), <i>o</i>-dppb (0.05 mol%), neat, 150°, microwave, 15 min</p>	<p>I (96)</p>	749
<p>(EtO)₂MeSiH (2.3 eq), CsF (1 eq), rt, 5 h</p>	<p>HO  II (100) + <i>n</i>-C₁₁H₂₃OH (0)</p>	83
<p>PMHS (3 eq), (C₆F₅)₃Br (5 mol%), CH₂Cl₂, rt, 5-20 min</p>	<p> II (86)</p>	354
<p>(EtO)₃SiH (1 eq), CsF, rt, 1 h</p>	<p>II (70)</p>	80
<p>PMHS (2.5 eq), (Ph₃P)CuH (3 mol%), MeC₆H₅, 22 h</p>	<p>II (78)</p>	317

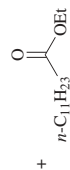


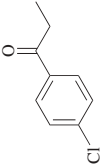
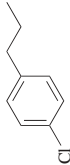
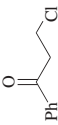

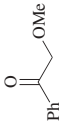
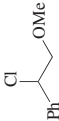
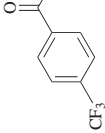
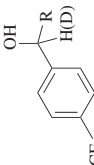

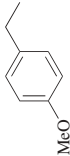
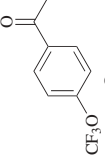
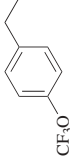
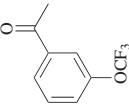
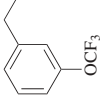


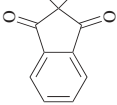

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

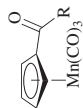
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	$(\text{EtO})_3\text{SiH}$ (2.3 eq), CsF (1 eq), rt, 0.5 h	 (70)	83
	PMHS (3 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 5-20 min	 (83)	354
	PMHS (3 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 5-20 min	 (84)	354
	Me_2ClSiH (1.2 eq), $\text{In}(\text{OH})_3$ (5 mol%), CHCl_3 , rt, 3.5 h	 (46)	331
	$\text{Et}_3\text{SiH(D)}$, $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , 0°	 (—)	751
	Me_2ClSiH (1.2 eq), $\text{In}(\text{OH})_3$ (5 mol%), CHCl_3 , rt, 3.5 h	 (38)	331
	Et_3SiH , TFA	 (—)	414
	Et_3SiH , TFA	 (—)	414

R = Me, CD_3

	Me_2ClSiH (1.2 eq), $\text{In}(\text{OH})_3$ (5 mol%), CHCl_3 , rt, 3.5 h	331
	Me_2ClSiH (4 eq), $\text{In}(\text{OH})_3$ (5 mol%), CHCl_3 , 60°, 3.5 h	331
	Me_2ClSiH (1.2 eq), $\text{In}(\text{OH})_3$ (5 mol%), CHCl_3 , rt, 3.5 h	331
	Et_3SiH (1.5 eq), $\text{CF}_3\text{SO}_3\text{H}$ (4 eq), CH_2Cl_2 , 0° to rt, 2 h	420
	Et_3SiH (2.6 eq), PPHF , TFA , 0°, 10 min, rt, 3 h	135
	Ph_2SiH_2 (1.2 eq), AlCl_3 (1 eq), CH_2Cl_2 , 20°, 18 h; 40°, 11 h	373
	R_3SiH (1.25 eq), AlCl_3 , CH_2Cl_2 , rt	90
	R_3Si	
	PhMe_2Si	
	Ph_3Si	
	Et_3Si	
	$\text{Me}(\text{EtO})_2\text{Si}$	
	$[-\text{Si}(\text{H})(\text{Me})\text{O}-]_4$	
	PhMe_2Si	
	Ph_3Si	
	$n\text{-Pr}$	
	$n\text{-Pr}$	
	$n\text{-Pr}$	
	$n\text{-Pr}$	
	Ph	
	Ph	

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

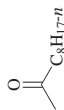
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																														
<div>C₉₋₁₆</div> <div></div>	Et ₃ SiH (5 eq), TFA (20 eq), 50°, 20 h	<div></div>	422																														
<table><tr><th>R¹</th><th>R²</th></tr><tr><td>H</td><td>H</td></tr><tr><td>H</td><td>Me</td></tr><tr><td>H</td><td>4-MeC₆H₄</td></tr><tr><td>H</td><td>4-BrC₆H₄</td></tr><tr><td>H</td><td>4-FC₆H₄</td></tr><tr><td>H</td><td>4-ClC₆H₄</td></tr><tr><td>H</td><td>4-IC₆H₄</td></tr><tr><td>Me</td><td>Me</td></tr><tr><td>Me</td><td>Ph</td></tr><tr><td>Me</td><td>Bn</td></tr><tr><td>Me</td><td>3-FC₆H₄</td></tr><tr><td>Me</td><td>3-ClC₆H₄</td></tr><tr><td>Me</td><td>3-BrC₆H₄</td></tr><tr><td>Et</td><td>3-BrC₆H₄</td></tr></table>	R ¹	R ²	H	H	H	Me	H	4-MeC ₆ H ₄	H	4-BrC ₆ H ₄	H	4-FC ₆ H ₄	H	4-ClC ₆ H ₄	H	4-IC ₆ H ₄	Me	Me	Me	Ph	Me	Bn	Me	3-FC ₆ H ₄	Me	3-ClC ₆ H ₄	Me	3-BrC ₆ H ₄	Et	3-BrC ₆ H ₄		<div>(80) (100) (87) (85) (93) (83) (79) (100) (20) (32) (21) (20) (20) (15)</div>	
R ¹	R ²																																
H	H																																
H	Me																																
H	4-MeC ₆ H ₄																																
H	4-BrC ₆ H ₄																																
H	4-FC ₆ H ₄																																
H	4-ClC ₆ H ₄																																
H	4-IC ₆ H ₄																																
Me	Me																																
Me	Ph																																
Me	Bn																																
Me	3-FC ₆ H ₄																																
Me	3-ClC ₆ H ₄																																
Me	3-BrC ₆ H ₄																																
Et	3-BrC ₆ H ₄																																

C₁₀₋₁₅

Et₃SiH (3 eq), TFA (5 eq),
40-50°

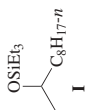
R	Time	
Me	15 h	(84)
CF ₃	15 h	(95)
Ph	15 h	(92)

351

C₁₀

Et₃SiH (5 eq), **121** (0.05 mol%),
CuCl (3 mol%), NaOBu-*t* (3 mol%),
MeC₆H₅

(87)



749

Et₃SiH (5 eq), CuCl (3 mol%),
NaOBu-*t* (3 mol%), **123** (0.05 mol%),
MeC₆H₅

1 (87)


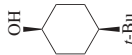

749

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																																					
<div>C₁₀</div> <div></div>	Et ₃ SiH (1.1 eq), acid, rt	<div></div> + <div></div> I + II (100) II I + II (72), I:II 18:82	74																																																					
	PMHS (2.5 eq), KF•2H ₂ O (1.25 eq), DMF, 60°, 3 h		82																																																					
	H , rt, 5 h	I + II (92), I:II 67:33	93																																																					
	G , 0°, 2 h	I (92), I:II 44:56	93																																																					
	R ₃ SiH (1.1 eq), acid catalyst (1 eq), 0° to rt, 24 h	I + II (~100)	72, 381																																																					
	<table><tr><th>R₃Si</th><th>Acid Catalyst</th><th>I:II</th></tr><tr><td><i>n</i>-BuH₂Si</td><td>BF₃•OEt₂</td><td>17:83</td></tr><tr><td><i>n</i>-BuH₂Si</td><td>TFA (6.8 eq)</td><td>16:84</td></tr><tr><td>Et₂HSi</td><td>BF₃•OEt₂</td><td>36:64</td></tr><tr><td>Et₃Si</td><td>BF₃•OEt₂</td><td>61:39</td></tr><tr><td>Et₃Si</td><td>H₂SO₄</td><td>10:90</td></tr><tr><td><i>n</i>-BuH₂Si</td><td>H₂SO₄</td><td>20:80</td></tr><tr><td>Et₂HSi</td><td>H₂SO₄</td><td>32:68</td></tr><tr><td>Et₃Si</td><td>TFA (6.8 eq)</td><td>32:68</td></tr><tr><td>(<i>n</i>-Bu)₃Si</td><td>H₂SO₄</td><td>22:78</td></tr><tr><td>(<i>n</i>-C₆H₁₃)₃Si</td><td>H₂SO₄</td><td>21:79</td></tr><tr><td><i>n</i>-PhH₂Si</td><td>TFA (2 eq)</td><td>20:80</td></tr><tr><td>(<i>i</i>-C₃H₁₁)₃Si</td><td>TFA (6.7 eq)</td><td>30:70</td></tr><tr><td>(<i>c</i>-C₅H₉)₃Si</td><td>TFA (7 eq)</td><td>44:56</td></tr><tr><td>(<i>i</i>-Bu)₃Si</td><td>TFA (7 eq)</td><td>55:45</td></tr><tr><td>(<i>s</i>-Bu)₃Si</td><td>TFA (0.9 eq)</td><td>56:44</td></tr><tr><td>(<i>s</i>-Bu)₃Si</td><td>TFA (7 eq)</td><td>55:45</td></tr><tr><td>(<i>t</i>-Bu)₃Si</td><td>TFA (7.2 eq)</td><td>68:32</td></tr></table>	R ₃ Si	Acid Catalyst	I:II	<i>n</i> -BuH ₂ Si	BF ₃ •OEt ₂	17:83	<i>n</i> -BuH ₂ Si	TFA (6.8 eq)	16:84	Et ₂ HSi	BF ₃ •OEt ₂	36:64	Et ₃ Si	BF ₃ •OEt ₂	61:39	Et ₃ Si	H ₂ SO ₄	10:90	<i>n</i> -BuH ₂ Si	H ₂ SO ₄	20:80	Et ₂ HSi	H ₂ SO ₄	32:68	Et ₃ Si	TFA (6.8 eq)	32:68	(<i>n</i> -Bu) ₃ Si	H ₂ SO ₄	22:78	(<i>n</i> -C ₆ H ₁₃) ₃ Si	H ₂ SO ₄	21:79	<i>n</i> -PhH ₂ Si	TFA (2 eq)	20:80	(<i>i</i> -C ₃ H ₁₁) ₃ Si	TFA (6.7 eq)	30:70	(<i>c</i> -C ₅ H ₉) ₃ Si	TFA (7 eq)	44:56	(<i>i</i> -Bu) ₃ Si	TFA (7 eq)	55:45	(<i>s</i> -Bu) ₃ Si	TFA (0.9 eq)	56:44	(<i>s</i> -Bu) ₃ Si	TFA (7 eq)	55:45	(<i>t</i> -Bu) ₃ Si	TFA (7.2 eq)	68:32	
R ₃ Si	Acid Catalyst	I:II																																																						
<i>n</i> -BuH ₂ Si	BF ₃ •OEt ₂	17:83																																																						
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Et ₂ HSi	BF ₃ •OEt ₂	36:64																																																						
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Et ₂ HSi	H ₂ SO ₄	32:68																																																						
Et ₃ Si	TFA (6.8 eq)	32:68																																																						
(<i>n</i> -Bu) ₃ Si	H ₂ SO ₄	22:78																																																						
(<i>n</i> -C ₆ H ₁₃) ₃ Si	H ₂ SO ₄	21:79																																																						
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(<i>i</i> -C ₃ H ₁₁) ₃ Si	TFA (6.7 eq)	30:70																																																						
(<i>c</i> -C ₅ H ₉) ₃ Si	TFA (7 eq)	44:56																																																						
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(<i>s</i> -Bu) ₃ Si	TFA (7 eq)	55:45																																																						
(<i>t</i> -Bu) ₃ Si	TFA (7.2 eq)	68:32																																																						

R ₃ SiH, Triton-B or TBAF	I + II (>90)	
	R ₃ Si	Catalyst
	PMHS	Triton-B
	(TMSO) ₃ Si	Triton-B
	(MeO) ₃ Si	Triton-B
	(EtO) ₃ Si	Triton-B
	PMHS	TBAF
	(TMSO) ₃ Si	TBAF
	(MeO) ₃ Si	TBAF
	(EtO) ₃ Si	TBAF
	PMHS (10% xs), [Bu ₂ (AcO)Sn] ₂ O (2 mol%), EtOH, reflux	
	II (65)	
	316	
	I + II (92), I:II = 33:67	
	390	
	Ph ₂ SiH ₂ (1.3 eq), 87 (5 mol%), RhCl ₃ (1 mol%), AgBF ₄ (2 mol%), THF, 0°, 1 d	

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																																												
<div>C₁₀ </div>	1. R ₃ SiH (1.5 eq), (Ph ₃ P) ₃ RhCl (2 mol%), C ₆ H ₆ 2. TsOH, aq. MeOH, rt, 1 h	<div></div> <div>(—) + <div></div></div>	391																																																												
	<table><tr><th>R₃Si</th><th>Temp</th><th>Time</th><th>I</th><th>I:II</th></tr><tr><td>Et₃Si</td><td>rt</td><td>144 h</td><td></td><td>33:67</td></tr><tr><td>Et₃Si</td><td>45°</td><td>20 h</td><td></td><td>23:77</td></tr><tr><td>Et₃Si</td><td>80°</td><td>3 h</td><td></td><td>11:89</td></tr><tr><td>Et₃Si</td><td>110°</td><td>1.5 h</td><td></td><td>12:88</td></tr><tr><td>Ph₃Si</td><td>rt</td><td>64 h</td><td></td><td>19:81</td></tr><tr><td>Ph₃Si</td><td>80°</td><td>24 h</td><td></td><td>12:88</td></tr><tr><td>PhMe₂Si</td><td>80°</td><td>12 h</td><td></td><td>29:71</td></tr><tr><td>(EtO)₃Si</td><td>80°</td><td>20 h</td><td></td><td>29:71</td></tr><tr><td>Cl₃Si</td><td>80°</td><td>18 h</td><td></td><td>37:63</td></tr><tr><td>Et₂HSi</td><td>rt</td><td>0.25 h</td><td></td><td>46:54</td></tr><tr><td>Ph₂HSi</td><td>rt</td><td>0.25 h</td><td></td><td>57:43</td></tr></table>	R ₃ Si	Temp	Time	I	I:II	Et ₃ Si	rt	144 h		33:67	Et ₃ Si	45°	20 h		23:77	Et ₃ Si	80°	3 h		11:89	Et ₃ Si	110°	1.5 h		12:88	Ph ₃ Si	rt	64 h		19:81	Ph ₃ Si	80°	24 h		12:88	PhMe ₂ Si	80°	12 h		29:71	(EtO) ₃ Si	80°	20 h		29:71	Cl ₃ Si	80°	18 h		37:63	Et ₂ HSi	rt	0.25 h		46:54	Ph ₂ HSi	rt	0.25 h		57:43	<div>1. R₃SiH (1.5 eq), (Ph₃P)₃RuCl₂ (2 mol%), I + II (60:90) C₆H₆, 80° 2. TsOH, aq. MeOH, rt, 1 h</div>	391
R ₃ Si	Temp	Time	I	I:II																																																											
Et ₃ Si	rt	144 h		33:67																																																											
Et ₃ Si	45°	20 h		23:77																																																											
Et ₃ Si	80°	3 h		11:89																																																											
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Ph ₃ Si	rt	64 h		19:81																																																											
Ph ₃ Si	80°	24 h		12:88																																																											
PhMe ₂ Si	80°	12 h		29:71																																																											
(EtO) ₃ Si	80°	20 h		29:71																																																											
Cl ₃ Si	80°	18 h		37:63																																																											
Et ₂ HSi	rt	0.25 h		46:54																																																											
Ph ₂ HSi	rt	0.25 h		57:43																																																											
	<table><tr><th>R₃Si</th><th>Time</th><th>I:II</th></tr><tr><td>Et₃Si</td><td>8 h</td><td>8:92</td></tr><tr><td>Et₃Si</td><td>20 h</td><td>5:95</td></tr><tr><td>Ph₃Si</td><td>24 h</td><td>7:93</td></tr><tr><td>PhMe₂Si</td><td>10 h</td><td>12:88</td></tr><tr><td>Et₂HSi</td><td>12 h</td><td>41:59</td></tr><tr><td>Ph₂HSi</td><td>12 h</td><td>49:51</td></tr></table>	R ₃ Si	Time	I:II	Et ₃ Si	8 h	8:92	Et ₃ Si	20 h	5:95	Ph ₃ Si	24 h	7:93	PhMe ₂ Si	10 h	12:88	Et ₂ HSi	12 h	41:59	Ph ₂ HSi	12 h	49:51																																									
R ₃ Si	Time	I:II																																																													
Et ₃ Si	8 h	8:92																																																													
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Et ₂ HSi	12 h	41:59																																																													
Ph ₂ HSi	12 h	49:51																																																													

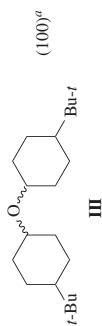
Ph₂SiH₂ (1.3 eq), (Ph₃P)₄RhH (0.3 mol%), **I** + **II** (81), **I:II** = 16:84
CH₂Cl₂, rt, 5 h

PhSiH₃ (0.4 eq), Mn(dpm)₃ (3 mol%), **I** + **II** (98), **I:II** = 1:1.4
i-PrOH, DCE, O₂, rt

Ph₂SiH₂ (1.5 eq), (Ph₃P)₃RhCl (1 mol%), **I** + **II**
ligand (2 mol%), AgBF₄ (2 mol%), THF

Ligand	Temp	Time	I + II	I:II
95	rt	4 h	(87)	35:65
87	0°	1 d	(92)	33:67
72	5°	4 h	(74)	39:61

Et₃SiH (2 eq), TMSOTf (0.1 eq),
CH₂Cl₂, rt, 2 h



Et₃SiH (1.1 eq), H₂SO₄, H₂O,
MeCN, 28°, 65 h

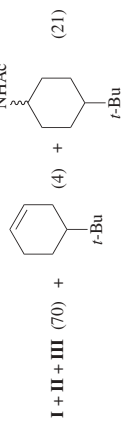


TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

C₁₀

Ketone

Conditions

Product(s) and Yield(s) (%)

Refs.

R₃SiH (x eq), TFA (y eq)

V

IV

VII

VI

VIII

IX

trans, trans cis, cis

R ₃ Si	x	y	IV + V	IV:V	VI + VII + VIII	VI (%)	VII (%)	VIII (%)
<i>n</i> -BuH ₂ Si	1.0	2.5	(26)	0.031	(74)	67	29	4
<i>n</i> -PrH ₂ Si	1.05	2.1	(50)	0.25	(50)	53	40	7
PMHS	0.8	6.8	(66)	0.23	(34)	30	55	15
Et ₃ Si	1.0	7.5	(83)	0.49	(17)	25	48	27
(<i>c</i> -C ₃ H ₇) ₃ Si	0.75	7.0	(89)	0.79	(11)	13	35	52
(<i>i</i> -Bu) ₃ Si	1.1	7.0	(86)	1.08	(14)	18	43	39
(<i>s</i> -Bu) ₃ Si	0.83	7.0	(94)	1.22	(6)	3	24	73

(4-*t*-Bu)₂SiH₂ (1 eq), TFA (6.6 eq), rt, 2 h

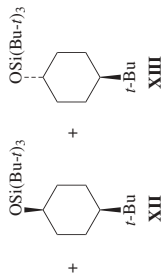
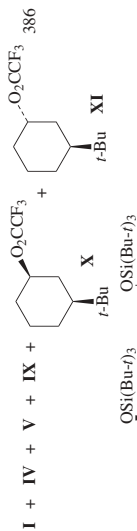
IV (66) + V (31) +

(3)

IX

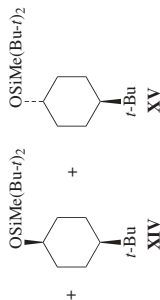
386

(*t*-Bu)₃SiH (1.2 eq), TFA (3 eq), rt




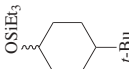



Time	% Conv.	I	IV	V	IX	X	XI	XII + XIII
21 h	50	(9)	(10)	(8)	(5.5)	(3)	(0.5)	(64)
27 h	53	(10)	(12)	(9.3)	(7.4)	(3.7)	(0.6)	(57)
93 h	85	(—)	(13)	(9)	(22)	(4.2)	(0.8)	(51)
264 h	94	(—)	(13)	(9.3)	(50)	(6.5)	(1.2)	(20)
720 h	97	(—)	(21)	(10)	(38)	(18)	(3)	(10)




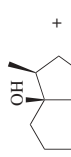
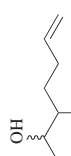
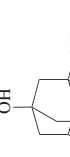

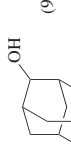


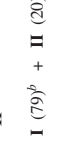





(*t*-Bu)₂MeSiH (1.17 eq), TFA (3 eq), rt



Time	IX	XIV	XV	I + IV	II + V
0.6 h	(0.7)	(70)	(27)	(1.8)	(0.5)
21 h	(6)	(41)	(18)	(27)	(7)
46 h	(8)	(28)	(10)	(38)	(16)
96 h	(8)	(27)	(8)	(39)	(20)

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₀		 (100) cis:trans = 32:68 XVI	74
Et ₃ SiH (1.1 eq), ZnCl ₂ (1.0 eq), rt			
Et ₃ SiH (1.1 eq), ZnCl ₂ (0.1 eq), rt		XVI (100) cis:trans = 67:33	74
Et ₃ SiH (1.1 eq), BF ₃ •OEt ₂ (3.0 eq), rt		XVI (100) cis:trans = 61:39	74
Et ₃ SiH (1.1 eq), SnCl ₂ (0.1 eq), rt		III (50) + XVI (50) cis:trans = 42:58	74
Et ₃ SiH (1.1 eq), AlCl ₃ (0.1 eq), rt		III (55) + XVI (55) cis:trans = 60:40	74
TBBSH (3 eq), TBSOTf (0.01 eq), rt, 2 h		 XVII + XVIII (81), XVII:XVIII 66:34	392
Et ₃ SiH (1.1 eq), HCO ₂ H (2.0 eq), rt		 (100) cis:trans = 38:62	74
Me ₂ ClSiH (1.2 eq), In(OH) ₃ (5 mol%), CHCl ₃ , 60°, 2 h		 (76) cis:trans = 12:88	331

			367
			428, 429
			243
			367
			1
			420
			217
			334

PhSiH₃ (0.4 eq), Mn(dpm)₃ (3 mol%),
i-PrOH, DCE, O₂, rt

PhMeSiH₂ Cp₂Ti(PMe₃)₂ (10 mol%),
PMe₃ (60 mol%), MeC₆H₅, -20°

Et₃SiH (1.5 eq), H₂SO₄/carbon,
n-C₈H₁₄, rt, 6 h

PhSiH₃ (0.4 eq), Mn(dpm)₃ (3 mol%),
i-PrOH, DCE, O₂, rt

1. BF₃, CH₂Cl₂, 0°

2. EtMe₂SiH (2.2 eq), 0°, 60 min

Et₃SiH (1.5 eq), CF₃SO₃H (4 eq),
CH₂Cl₂, 0° to rt, 2 h

Et₃SiH (1.3 eq), BF₃•OEt₂ (4-6 eq),
CH₂Cl₂, rt, 1 h

Et₃SiH (2 eq), TMSOTf (0.1 eq),
CH₂Cl₂, rt, 2 h

I + II:III = 6:1, I:II = 70:1, I + III (72)

(95)

(99)

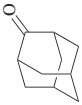
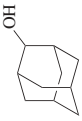

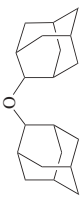
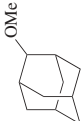
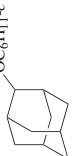
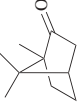


(100)

I (79)^b + II (20)^b

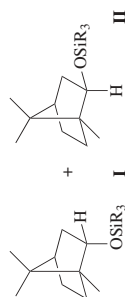
II (78)

(100)^a

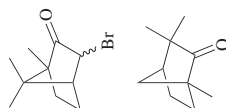
TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₀	TMSH (xs), 220 (0.09 eq), Ph ₃ CCl (0.1 eq), CH ₂ Cl ₂ , rt, 2 h,	 I +  II +  III I + II + III (98), I:II:III = 8:15:75	424
	TMSH (xs), TMSCl (cat.), Ph ₃ CH (0.1 eq), 220 (0.09 eq), CH ₂ Cl ₂ , rt, 2 h	I + II + III (75), I:II:III = 26:40:29	424
	1. HC(OMe) ₃ , CH ₂ Cl ₂ , rt, 2 h 2. Et ₃ SiH, Nafion [®] -H, CH ₂ Cl ₂ , reflux, 3 h	 (93)	335
	Et ₃ SiH, TMSOTf, TMSI, <i>c</i> -C ₆ H ₁₁ OTMS, CH ₂ Cl ₂ , 0°, 2 h	 (100) ^{4a}	334
	(EtO) ₃ SiH (1 eq), CsF, rt, 1 min	 I (95)	80
	PhSiH ₃ (0.4 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE, O ₂ , rt	I (trace)	367
	Et ₃ SiH (1 eq), TMSOTf (1 eq), <i>n</i> -C ₆ H ₁₃ OTMS (0.83 eq), CH ₂ Cl ₂ , 0° to rt	 (88)	341

R_3SiH , $(Ph_3P)_3RhCl$, solvent, 0-80°			
R_3Si	mmol Cat.	Solvent	
Ph_3Si	0.1	none	
Et_2HSi	0.1	none	
$PhMeHSi$	0.1	none	
Ph_2HSi	0.1	none	
Et_3Si	1.0	hexane	
$PhMe_2Si$	0.1	none	



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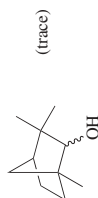


$(EtO)_3SiH$ (1.1 eq), CsF (1 eq), 70°, 3 h



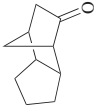
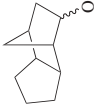
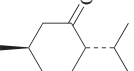
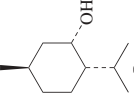




79, 80

$PhSiH_3$ (0.4 eq), $Mn(dpm)_3$ (3 mol%),
i-PrOH, DCE; O_2 , rt



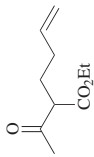
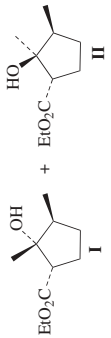
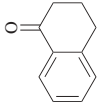
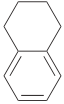

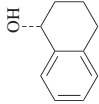


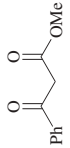
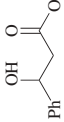
367

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. HC(OMe)_3 , CH_2Cl_2 , rt, 2 h 2. Et_3SiH , Nafion [®] -H, CH_2Cl_2 reflux, 3 h	 (88)	335
	R_3SiH , $(\text{Ph}_3\text{P})_3\text{RhCl}$, solvent, 0-80°	 I  II	387, 388
	R_3Si mol% Cat. Solvent	I II	
	Ph_3Si 0.1 none	(90) (10)	
	Et_2HSi 0.1 none	(83) (17)	
	PhMeHSi 0.1 none	(86) (14)	
	Ph_2HSi 0.1 none	(85) (15)	
	Et_3Si 1.0 hexane	(64) (36)	
	PhMe_2Si 0.1 none	(0) (0)	
	PhMe_2SiH (1.2 eq), [$\text{Rh}(\text{C}_2\text{H}_4)_2$] ₂ (0.5 mol%), $\text{P}(\text{tm-ap})_3$ (2 mol%), C_6H_6 , rt, 20 h	I + II (92), I:II 45:55	389
	R_3SiH (1.1 eq), acid catalyst (1 eq), 0° to rt, 24 h	 I  II	384
	R_3Si Acid Catalyst	I:II	
	<i>n</i> -BuH ₂ Si HOAc	18:82	
	Et_3Si HOAc	39:61	
	Et_3Si $\text{BF}_3\cdot\text{OEt}_2$	64:36	

	<p>Ph₃SiH (4 eq), catalyst (2.2 eq), CH₂Cl₂, -78°, 6 h; 0°, 12 h</p>	<p>I + II I:II (81) >99:1 (47) —</p>	407
	<p>Catalyst BF₃•OEt₂ TMSOTf</p>	<p>I + II I:II (82) 250:1 (47) —</p>	397
	<p>1. (<i>i</i>-Pr)₂SiClH, Et₃N, DMAP, hexane 2. SnCl₄, CH₂Cl₂, -80°</p>	<p>I + II (82), I:II 250:1 I + III (75), I:III = 300:1</p>	397
	<p>1. (<i>i</i>-Pr)₂SiClH, Et₃N, DMAP, hexane 2. SnCl₄, CH₂Cl₂, -80°</p>	<p>I + III (75), I:III = 300:1</p>	397
	<p>(EtO)₃SiH (2.3 eq), CsF (1 eq), rt, 10 min</p>	<p>I + III (75), I:III = 300:1</p>	80, 83
	<p>PhM₂SiH (1.2 eq), TFA, 0°, 6 h</p>	<p>I + II (91), I:II = 2:98</p>	87, 276
	<p>PhM₂SiH (1.2 eq), TASf (10 mol%), DMPU, 0°, 22 h</p>	<p>I + II (93), I:II 23:77</p>	87, 276

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph_2SiH_2 (1.0 eq), $\text{Cp}_2\text{Ti}(\text{PPh}_3)_2$, MeC_6H_5 , 21°	 I (78), I + II : III = 99:1 II = 90:1	428
	Et_3SiH (1.3 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (4-6 eq), CH_2Cl_2 , rt, 6 h	 (67)	217
	$(\text{MeO})_3\text{SiH}$ (1 eq), Et_2O :TMEDA (30:1), Li-(<i>R</i>)-BINOL (10 mol%), 0° , 24 h	 (39) 93% ee	592
	Silane, Triton-B	 I + II (>90) I : II	278
	Ph_2SiH_2 (1.2 eq), AlCl_3 (1 eq), CH_2Cl_2 , 20° , 20 h	 (90) + Ph_2HSiCl (—)	373

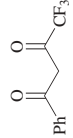
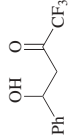
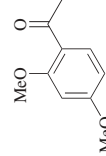
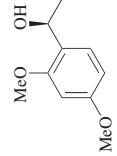
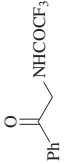
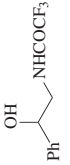
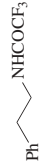
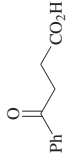
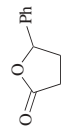
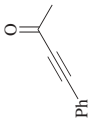
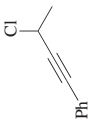
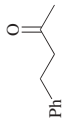
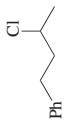
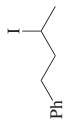
		Ph_2SiH_2 (1.2 eq), AlCl_3 (1 eq), CH_2Cl_2 , 20°, 22 h	(30) + Ph_2SiHCl (—)	373
		TBSH (1.2 eq), 123 (0.1 mol%), CuCl (0.5 mol%), $\text{NaOBu-}t$ (3 mol%), MeC_6H_5 , rt, 4 h	(90) ^b 80% ee	749
		Et_3SiH (3.42 eq), TFA, reflux, 2 h; rt, 16 h	(50)	376
		Et_3SiH (4 eq), $\text{BF}_3\cdot\text{OEt}_2$ (20 eq), reflux, 2 h; rt, 16 h	(78)	376
		Et_3SiH (2.2 eq), TFA, rt	(86) + $\text{Ph-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ (14)	73
		Me_2ClSiH (1.2 eq), In(OH)_3 (5 mol%), CHCl_3 , 0°, 0.3 h	(78)	331
		Me_2ClSiH (1.2 eq), In(OH)_3 (5 mol%), CHCl_3 , 60°, 3 h	(92)	331
		Me_2ClSiH (1.2 eq), In(OH)_3 (5 mol%), LiI , CHCl_3 , rt, 11 h	(74)	331

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₁₀₋₂₃</div> <div></div>	PMHS, (2-2.5 eq), TBAF (1 eq), THF, 0-5°, 2 h	<div></div> <div>I</div> <div>II</div> <div>I + II</div> <div>I:II</div> <div>(77) 87:13</div> <div>(79) 73:27</div> <div>(76) 97:3</div> <div>(76) 100:0</div> <div>(80) 100:0</div> <div>(88) 26:74</div> <div>(71) 97:3</div> <div>(87) 100:0</div> <div>(90) 95:5</div> <div>(95) 100:0</div>	401
<div>C₁₁</div> <div></div>	Ph ₂ MeSiH (2 eq), TMSOTf (1 eq), CH ₂ Cl ₂ , 0°, 2 h	<div></div> <div>(50) trans:cis = 1:1</div>	336
<div></div>	Ph ₃ SiH (4 eq), BF ₃ •OEt ₂ (2.2 eq), CH ₂ Cl ₂ , -78° to 20°, 12 h	<div></div> <div>(81) cis:trans > 20:1</div>	407
<div></div>	PMHS (1.2 eq), KF•2H ₂ O (1.3 eq), DMF, 30°, 5 h	<div></div> <div>(59)</div>	82

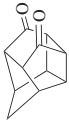
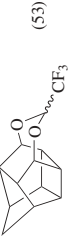
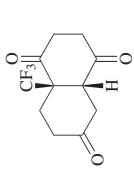
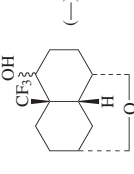
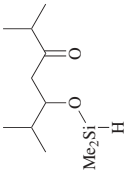
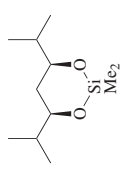

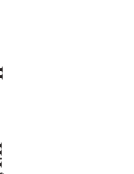
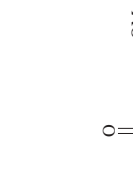

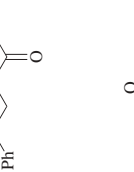

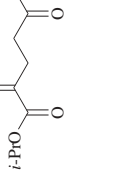



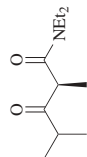
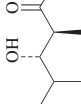
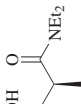
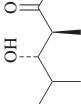
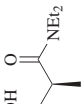
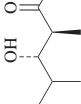
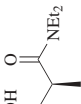
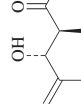
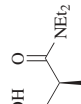
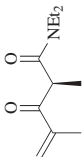
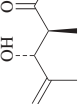
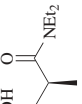
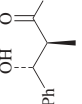
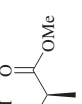
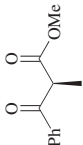
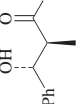
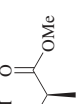
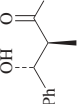
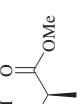
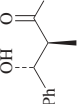
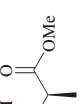
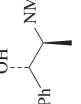
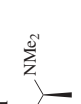
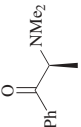
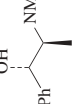
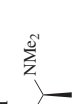
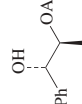
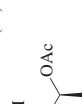
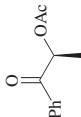
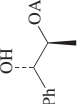
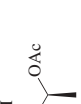
		<p>Et₃SiH (4 eq), TFA (36 eq), 20°, 20 min</p>	409
		<p>PMHS, TFA, rt, 2 d</p>	410
		<p>SnCl₄ (0.1 eq), -80°, 2 h</p>	399
		<p>MgBr₂•OEt₂ (0.1 eq), rt, 24 h</p>	399
		<p>BF₃•OEt₂ (0.5 eq), -80°, 2 h</p>	399
		<p>ZnBr₂ (0.12 eq), -80°, 8 h; rt, 16 h</p>	399
		<p>ZnCl₂ (0.25 eq), -80°, 30 min; rt, 15 min</p>	399
		<p>TFA (0.2 eq), -80°, 30 min</p>	399
		<p>Me(BiO)₂SiH (1 eq), CsF, rt, 2.5 h</p>	80, 83
		<p>Me(BiO)₂SiH (2.3 eq), CsF, rt, 2.5 h</p>	83
		<p>(EtO)₃SiH (1 eq), CsF, rt, 0.5 h</p>	79, 80

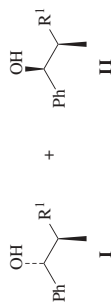
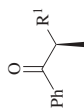
TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMe ₂ SiH (1.2 eq), TFA, 0°, 20 h	  I + II (89), I:II = 1:99   II	87, 276
	PhMe ₂ SiH (1.2 eq), TASF (10 mol%), DMPU, 0°, 24 h; rt, 72 h	  I + II (27), I:II = 25:75   II	87, 276
	PhMe ₂ SiH (1.2 eq), TFA, 0°, 16 h	  I + II (65), I:II < 1:99   II	87, 276
	PhMe ₂ SiH (1.2 eq), TFA, 0°, 3 h	  I + II (87), I:II < 1:99   II	87
	PhMe ₂ SiH (1.2 eq), TASF (10 mol%), DMPU, rt, 12 h	  I + II (—)   II	87, 276
	PhMe ₂ SiH (1.1-1.2 eq), TBAP (5-10 mol%), HMPA, rt, 12 h	  I + II (83) threo:erythro >99:1   II	86
	PhMe ₂ SiH (1.1-1.2 eq), TBAP (5-10 mol%), HMPA, 0°, 20 h	  I + II (95) threo:erythro = 95:5	86, 320

1. PhMe ₂ SiH (1.2 eq), TBAF (5-10 mol%), HMPA, 0°, 12 h 2. H ₂ O	 I + II (86) threo:erythro = 84:16	86, 320																		
(EtO) ₃ SiH (1 eq), CsF, rt, 2 h	 (75)	80																		
1. Ph ₂ SiH ₂ , Cp ₂ Ti(PMe ₃) ₂ (10 mol%), PMe ₃ (60 mol%), MeC ₆ H ₅ , -20° 2. TBAF, THF, 15 min	 I + II (86), (I + II):III = 99:1, I:II = 99:1	428, 429																		
1. Ph ₂ SiH ₂ , Cp ₂ Ti(PMe ₃) ₂ (10 mol%), PMe ₃ (60 mol%), MeC ₆ H ₅ , -20° 2. HCl/acetone, 3 h	 I (86), (I + II):III = 99:1, I:II = 99:1	428, 429																		
Et ₃ SiH (10 eq), TFA (x eq), BF ₃ •OEt ₂ (y eq), 20°	 (71)	211																		
<table><tr><th>x</th><th>y</th><th>Time</th></tr><tr><td>50</td><td>0</td><td>5 min</td></tr><tr><td>50</td><td>0</td><td>30 min</td></tr><tr><td>50</td><td>0</td><td>2 h</td></tr><tr><td>28</td><td>0.6</td><td>5 min</td></tr><tr><td>28</td><td>0.6</td><td>1 h</td></tr></table>	x	y	Time	50	0	5 min	50	0	30 min	50	0	2 h	28	0.6	5 min	28	0.6	1 h	 (30) (64) (70) (89) (90)	
x	y	Time																		
50	0	5 min																		
50	0	30 min																		
50	0	2 h																		
28	0.6	5 min																		
28	0.6	1 h																		
Et ₃ SiH (5 eq), TFA (9 eq), 50°, 30 h	 (75)	257																		
Et ₃ SiH (1.5 eq), CF ₃ SO ₃ H (4 eq), CH ₂ Cl ₂ , 0° to rt, 2 h	 (84)	420																		

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁			
	Me ₂ ClSiH (1.2 eq), In(OH) ₃ (5 mol %), CHCl ₃ , rt, 3.5 h	 (46)	331
	Me ₂ ClSiH (1.2 eq), In(OH) ₃ (5 mol %), CHCl ₃ , rt, 2 h		331
	Et ₃ SiH, TFA, LiClO ₄ (0.01 eq), rt, 4 h		423
C ₁₁₋₁₃			
	1. TMSiCl, Et ₃ N 2. PhMe ₂ SiH, TiCl ₄ , CH ₂ Cl ₂ , -78° to rt	 I + II	421
Ar		I + II	
Ph		(97)	94:6
4-ClC ₆ H ₄		(95)	98:2
		(95)	>99:1

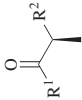
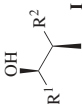
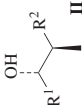


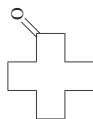
R₃SiH (1.1-1.2 eq),
TBAF (5-10 mol%), HMPA

320

R ¹	R ₃ Si	Temp	Time	I + II	I:II
OAc	PhMe ₂ Si	0°	20 h	(95)	95:5
OAc	PhMe ₂ Si	0°	4 h	(93)	93.3:6.7
OAc	(4-CF ₃ C ₆ H ₄)Me ₂ Si	0°	4 h	(72)	93.1:6.9
OAc	(4-MeC ₆ H ₄)Me ₂ Si	0°	4 h	(83)	93.1:6.9
OAc	(4-MeOC ₆ H ₄)Me ₂ Si	0°	4 h	(88)	93:7
OAc	PhMe ₂ Si	rt	14 h	(99)	93:7
OAc	Ph ₂ MeSi	rt	14 h	(89)	92:8
OAc	(<i>i</i> -PrO)Ph ₂ Si	rt	3 h	(91)	86:14
OAc	(<i>i</i> -PrO) ₃ Si	-50°	12 h	(71)	78:22
OBz	PhMe ₂ Si	0°	6 h	(82)	96:4
OEE	PhMe ₂ Si	0°	18 h	(55)	90:10

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

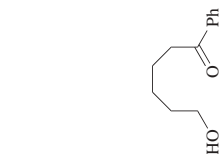
Ketone		Conditions	Product(s) and Yield(s) (%)		Refs.
C ₁₁₋₁₆					276
		PhMe ₂ SiH (1.1-1.2 eq), acid			
	R ¹	R ²	Acid	Temp	I + II I:II
	Ph	CO ₂ Me	TMSOTf (1 eq)	rt	(83) 79:21
	Ph	CO ₂ Me	AlCl ₃ (1 eq)	rt	(66) 78:22
	Ph	NMe ₂	TFA	rt	(0) —
	Ph	NHCO ₂ Me	TFA	0°	(87) >99:1
	Ph	NHCO ₂ Et	TFA	0°	(87) >99:1
	Ph	NHCO ₂ Et	AlCl ₃ (1 eq)	0°	(64) 70:30
	Ph	NHCO ₂ Et	TMSOTf (1 eq)	0°	(65) 71:29
	2,5-(MeO) ₂ C ₆ H ₃	NHCO ₂ Me	TFA	0°	(84) >99:1
	<i>n</i> -Bu	OBn	TFA	0°	(82) 47:53
	Ph	NHSO ₂ Ph	TFA	0°	(66) 98:2
	Ph	OBz	TFA	0°	(72) 93:7



TMSh (xs), **220**-TFPB (0.09 eq),
Ph₃CH (0.1 eq), CH₂Cl₂, rt, 2 h

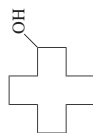
(91) cis:trans = 40:60

424

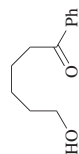


PhSiH₃ (0.4 eq), Mn(dpm)₃ (3 mol%),
i-PrOH, DCE, O₂, rt

(13)

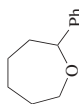


367

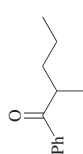


Ph₂MeSiH (2 eq), TMSOTf (1 eq),
CH₂Cl₂, 0°, 2 h

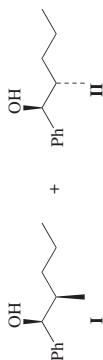
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336

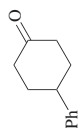


Et₃SiH, B(C₆F₅)₃ (2 mol%),
MeC₆H₅, 0°, 1 h

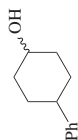


I + II (98), **I:II** = 1:1.5

372

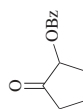


Cl₃SiH (1.5 eq),
CH₂Cl₂:DMF (4:1), 0°, 12 h

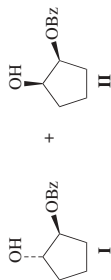


(85)

318



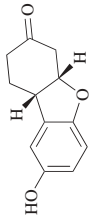
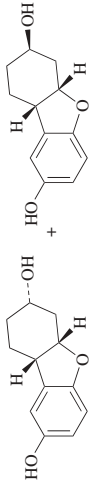
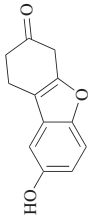
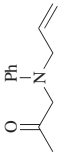
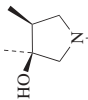
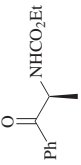

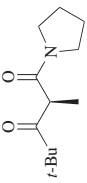

PhMe₂SiH (1.1-1.2 eq),
TBAF (5-10 mol%), HMPA, 0°, 4 h



I + II (76), **I:II** = 33:67

320

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et ₃ SiH (3.2 eq), TFA, 0°, 1 h	 I + II (56), I:II = 1:4	394
	Et ₃ SiH (3.2 eq), TFA, rt, 24 h	I + II (77), I:II = 4:1	394
	Ph ₃ SiH ₂ , Cp ₂ Ti(PMe ₃) ₂ (10 mol %), PMe ₃ (60 mol %), MeC ₆ H ₅ , -20°	 I + II + III (75), I + II : III = 99:1, I:II = 1:1	428, 249
	PhMe ₂ SiH (1.2 eq), TFA, 0°, 2.5 h	 (87) threo:erythro > 99:1	86
	PhMe ₂ SiH (1.2 eq), TASF (10 mol %), DMPU, 0°, 16 h	 I + II (90), I:II = 91:9	320

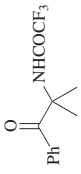

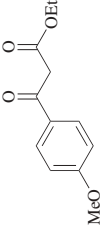
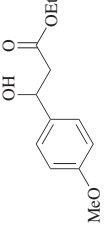
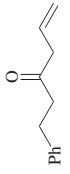

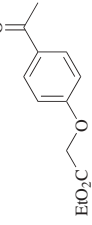
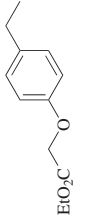
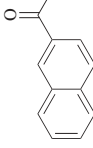
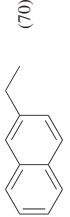
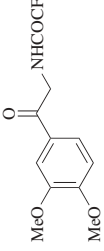
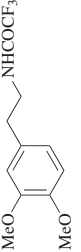
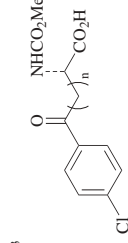
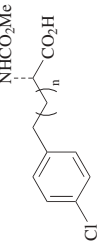
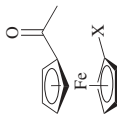
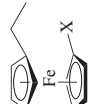
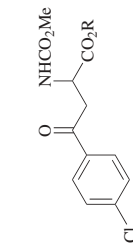
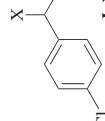
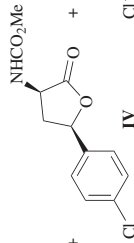
		Et_3SiH (3.42 eq), TFA, reflux, 2 h; rt, 16 h	(72)	376
		Ph_2SiH_2 (1.2 eq), AlCl_3 (1 eq), CH_2Cl_2 , 20°, 18 h; 40°, 4 h	(78) + Ph_2HSiCl (—)	373
		PMHS (3 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 5-20 min	(88)	354
		PMHS (3 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 5-20 min	(82)	354
		Et_3SiH (2.6 eq), $\text{BF}_3\cdot\text{OH}_2$ (4-6 eq), CH_2Cl_2 , rt, 10 h	(70)	217
		Et_3SiH (3.42 eq), TFA, reflux, 2 h, rt, 16 h	(74)	376
		1. TMSCl, Et_3N 2. Et_3SiH , TiCl_4 , CH_2Cl_2 , 0°, rt	n = 1 (89) n = 2 (85)	421, 752

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.					
<div>C₁₂₋₁₄</div> 	Et ₃ SiH (2.5 eq), TFA (5 eq), 20°	<div></div> <div>X</div> <div>H (40)</div> <div>Cl (45)</div> <div>CO₂Me (65)</div> <div>CN (85)</div>	180					
<div>C₁₂₋₁₅</div> 	Et ₃ SiH, acid, solvent	<div></div> <div>X NHC(OMe)₂Me</div> <div>CO₂R + Cl-Ph-Cl</div> <div>I: X = H III</div> <div>II: X = Cl</div> <div></div> <div>+ NHC(OMe)₂Me</div> <div>CO₂R + Cl-Ph-Cl</div> <div>IV V</div>	421					
R	Acid	Solvent	Temp	I	II	III	IV	V
H	TFA	none	reflux	(—)	(—)	(—)	(54)	(7)
Me	TFA	none	reflux	(25)	(—)	(—)	(49)	(10)
H	BF ₃ •OEt ₂	none	70°	(—)	(—)	(—)	(65)	(6)
Me	BF ₃ •OEt ₂	none	rt	(12)	(—)	(28)	(—)	(—)
H	TiCl ₄	CH ₂ Cl ₂	rt	(67)	(—)	(—)	(—)	(—)
Me	TiCl ₄	CH ₂ Cl ₂	rt	(25)	(38)	(—)	(—)	(—)
TMS	TiCl ₄	CH ₂ Cl ₂	rt	(88)	(—)	(—)	(—)	(—)
TMS	AlCl ₃	CH ₂ Cl ₂	rt	(45)	(—)	(23)	(—)	(—)
TMS	SnCl ₄	CH ₂ Cl ₂	rt	(—)	(—)	(—)	(—)	(—)



310, 425

Et₃SiH (x eq), TFA (y eq),
THF, reflux, 6 h

R	x	y
Me	2.4	2.07
Et	2.33	2
<i>n</i> -Pr	2.33	2
<i>i</i> -Pr	2.67	3.0
<i>n</i> -Bu	2.33	2
<i>n</i> -C ₆ H ₁₃	2.67	2.67
<i>c</i> -C ₆ H ₁₁	2.5	3.0
Ph	2.5	2.5
4-MeC ₆ H ₄	2.6	3.0
4-BrC ₆ H ₄	2.4	2.07

(90)
(92)
(87)
(81)
(80)
(80)
(75)
(82)
(78)
(67)

310

Et₃SiH (x eq), CO, C₆H₆, reflux, 8 h

R	x
Me	1.1
Me	1.06
Et	1.07
<i>n</i> -Pr	1.07
<i>i</i> -Pr	1.0
<i>n</i> -Bu	1.02
<i>n</i> -C ₆ H ₁₃	1.02
<i>c</i> -C ₆ H ₁₁	1.02
Ph	1.37
4-MeC ₆ H ₄	1.02
4-BrC ₆ H ₄	1.02

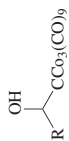
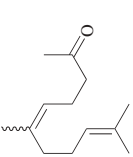
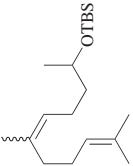
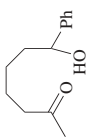
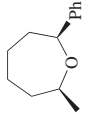
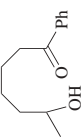

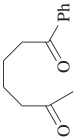




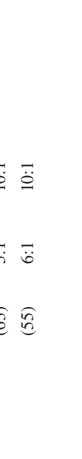
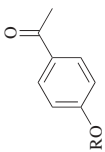
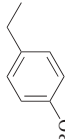
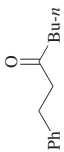



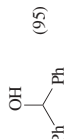
(84)
(90)
(73)
(75)
(80)
(81)
(81)
(52)
(87)
(70)
(84)

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

	TBBSH (1.2 eq), 123 (0.1 mol%), CuCl (3 mol%), NaOMe (3 mol %), Et ₂ O, rt, <3 h		749
	Et ₃ SiH (10 eq), TMSOTf (1 eq), CH ₂ Cl ₂ , 0°, 15 min		336
	Ph ₂ MeSiH (2 eq), TMSOTf (1 eq), CH ₂ Cl ₂ , 0°, 2 h		336
	Et ₃ SiH (10 eq), TMSOTf (1 eq), CH ₂ Cl ₂ , 0°, 15 min		336
	Ph ₂ MeSiH (2 eq), TMSOTf (1 eq), CH ₂ Cl ₂ , 0°, 2 h		336
	Ph ₂ SiH ₂ (1.0 eq), Cp ₂ Ti(PPh ₃) ₂ , MeC ₆ H ₅		428, 429

Temp	II	(II + III):I	II:III
-20°	(63)	2.2:1	99:1
-5°	(59)	3:1	65:1
0°	(50)	3.5:1	46:1
21°	(63)	5:1	10:1
50°	(55)	6:1	10:1

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃₋₁₄ 	PMHS (3 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 5-20 min	<div style="display: flex; align-items: center; justify-content: center;">  <div style="margin-left: 10px;"> R <div style="display: flex; justify-content: space-around; width: 100px;"> <div>THP (84)</div> <div>TBS (90)</div> </div> </div> </div>	354
C ₁₃ 	PMHS (3 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 5-20 min		354
	PMHS (3 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 5-20 min		354
	Et ₃ SiH (2.5 eq), TFA (5 eq), 20°	I (65)	180
	Et ₃ SiH (1.3 eq), NH ₄ F (1.3 eq), TFA (5 eq), 0°, 0.5 h; rt, 24 h	I (93)	135
	Et ₃ SiH (3.7 eq), 220 (0.09 eq), Ph ₃ CCl (0.1 eq), CH ₂ Cl ₂ , rt, 2 h	I (87)	424
	(EtO) ₃ SiH (2.3 eq), CsF (1 eq), rt, 5 min		83
	Me(EtO) ₂ SiH (2.3 eq), KF (1 eq), DMF, 20°, 0.5 h	II (90)	83
	R ₃ SiH (1 eq), MF	II	80, 83
	R ₃ Si MF Temp Time		
	Me(EtO) ₂ Si CsF rt 1.5 h	(75)	
	(EtO) ₃ Si KF 100° 10 h	(95)	
	(EtO) ₃ Si CsF 0° 5 min	(95)	

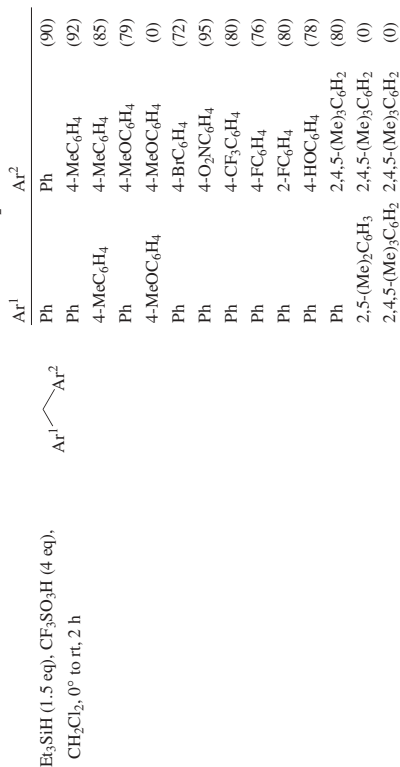
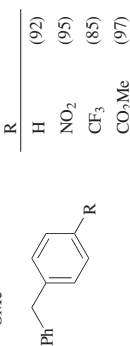
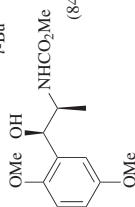
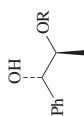
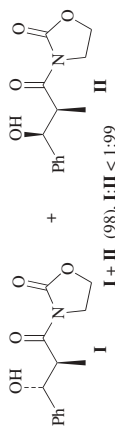
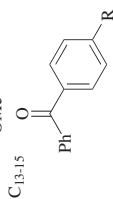
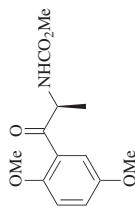
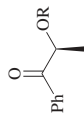
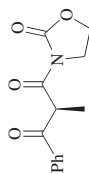
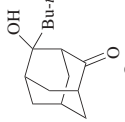
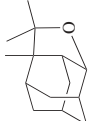
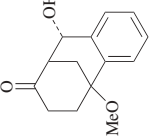
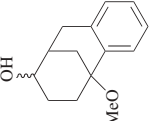
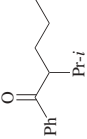

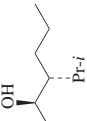
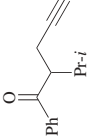
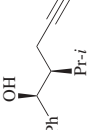
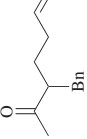

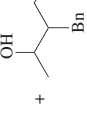
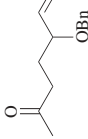

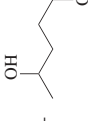


TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄ 	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 16 h	(77) 	153
	Et ₃ SiH, TFA	(75) 	716
	Et ₃ SiH, (C ₆ F ₅) ₃ B (2 mol%), MeC ₆ H ₅ , 0°, 1 h	 +  I + II (—), I:II = 98:2 II	372
	Et ₃ SiH, (C ₆ F ₅) ₃ B (2 mol%), MeC ₆ H ₅ , 0°, 1 h	(99) 	372
	Ph ₃ SiH ₂ (1.0 eq), Cp ₂ Ti(PPh ₃) ₂ , PPh ₃ (0.6 eq), MeC ₆ H ₅	 +  I + II (71), (I + II):III = 99:1, I:II = 20:1	428
	Ph ₃ SiH ₂ (1.0 eq), Cp ₂ Ti(PPh ₃) ₂ , PPh ₃ (0.6 eq), MeC ₆ H ₅ , 21°	 +  I + II + III (50), (I + II):III = 3:1, I:II = 3:2	428

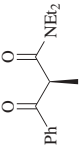
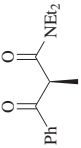


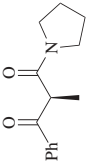
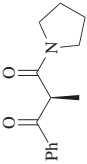
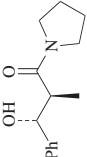
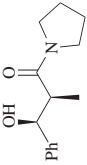
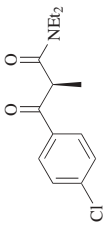
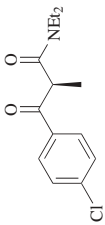
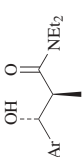
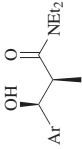
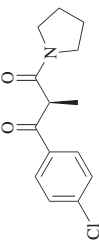
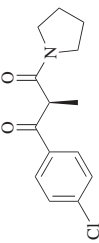
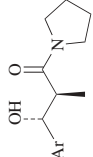
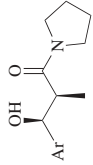
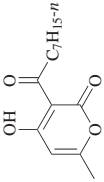
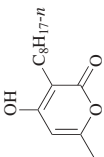


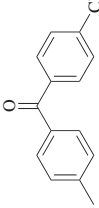
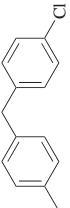
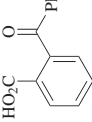
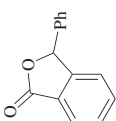

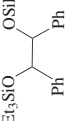
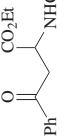
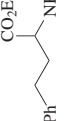
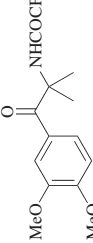
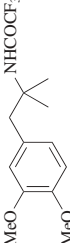
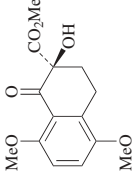
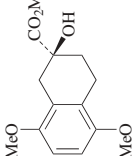
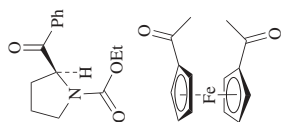
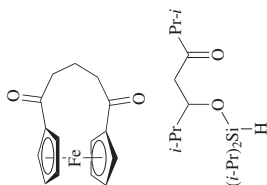
	Ph_2SiH_2 (1.0 eq), $\text{Cp}_2\text{Ti}(\text{PPh}_3)_2$, PPh_3 (0.6 eq), MeC_6H_5 , -20°	I + II (45), I:II = 8.5:1, I:II:III = 4:1.6:1	428
	PhMe_2SiH (1.2 eq), TASF (10 mol%), DMPU, 0° , 12 h	 +  I + II (98), I:II > 99:1 II	87, 320
	PhMe_2SiH (1.2 eq), TFA, 0° , 4 h	I + II (98), I:II < 1:99	87, 276
	PhMe_2SiH (1.2 eq), TASF (10 mol%), DMPU, 0° , 22 h	 +  I + II (98), I:II > 99:1 II	87, 320
	PhMe_2SiH (1.2 eq), TFA, 0° , 3 h	I + II (99), I:II < 1:99	87, 276
	PhMe_2SiH (1.2 eq), TASF (10 mol%), DMPU, 0° , 16 h	 +  I + II (86), I:II = 99:1 II Ar = 4-ClC₆H₄	87
	PhMe_2SiH (1.2 eq), TFA, 0° , 4 h	I + II (99), I:II < 1:99	87, 276
	PhMe_2SiH (1.2 eq), TASF (10 mol%), DMPU, 0° , 16 h	 +  I + II (98), I:II > 99:1 II Ar = 4-ClC₆H₄	320
	Et_3SiH , TFA, LiClO_4 (0.01 eq), rt, 4 h	 (88)	423

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. SbCl_5 , TMSCl , SnI_2 , CH_2Cl_2 , -78° , 30 min 2. Et_3SiH (1.5 eq), -23° , 2.5 h	 (90)	306
	PMHS (3 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 5-20 min	 (85)	354
	Et_3SiH (2.2 eq), TFA, rt	 (100)	73
	Et_3SiH (2.5 eq), $(\text{Ph}_3\text{P})_3\text{RhCl}$ (0.5 mol%), C_6H_{14} , 70° , 4 h	 (83)	411
	Et_3SiH (3.66 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (20 eq), rt, 48 h	 (22)	753
	Et_3SiH (4 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (20 eq), reflux, 2 h; rt, 16 h	 (78)	753
	Et_3SiH (3.0 eq), TFA, 0° to rt, 16 h	 (75)	416



C₁₅



Et₃SiH, TFA

Et₃SiH (2 eq), TFA, rt, 120 h

Et₃SiH (20 eq), TFA, rt, 20 h

Et₃SiH (4 eq), TFA, rt, 4 h

SnCl₄ (0.1 eq), -80°, 2 h

MgBr₂•OEt₂ (0.1 eq), rt, 24 h

TiCl₄ (0.5 eq), -80°, 30 min

BF₃•OEt₂ (0.5 eq), -80°, 2 h

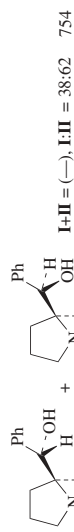
ZnBr₂ (0.12 eq), -80°, 8 h; rt, 16 h

ZnCl₂ (0.25 eq), -80°, 30 min; rt, 15 min

TFA (0.2 eq), -80°, 30 min

TBAF (0.2 eq), -80°, 30 min

(Ph₃P)₃RhCl (0.08 eq), C₆H₆, reflux, 12 h



I+II = (—), EII = 38:62

754

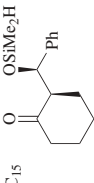
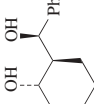
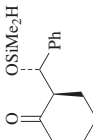
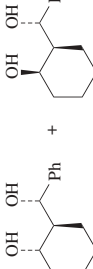






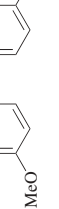





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TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₅	DMF, 100°, 24 h	 (67)	400
	DMF, 100°, 24 h	 I + II (26), I:II = 1:4	400
	1. SbCl ₅ , TMSCl, SnI ₂ , CH ₂ Cl ₂ , -78°, 30 min 2. Et ₃ SiH (1.5 eq), -23°, 2.5 h	 (68)	306
	1. Tr-SbCl ₆ (5-30 mol%), CH ₂ Cl ₂ , -78°, 30 min 2. Et ₃ SiH (1.5 eq), -23°, 2.5 h	 I (77)	306
	1. SbCl ₅ , TMSCl, SnI ₂ , CH ₂ Cl ₂ , -78°, 30 min 2. Et ₃ SiH (1.5 eq), -23°, 2.5 h	 (92)	306
	1. Tr-SbCl ₆ (5-30 mol%), CH ₂ Cl ₂ , -78°, 30 min 2. Et ₃ SiH (1.5 eq), -23°, 2.5 h	 I (96)	306
	Et ₃ SiH (2.5 eq), TFA (5 eq), 20°	 I (75)	180
	Et ₃ SiH (5 eq), Sn-mont, DCE, reflux, 20 h	 I (54)	353
	Et ₃ SiH (5 eq), CF ₃ SO ₃ H (1 eq), DCE, reflux, 10 h	 I (54)	353

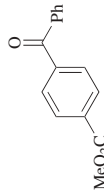
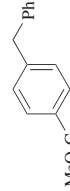
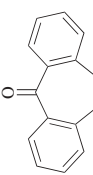
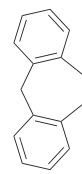
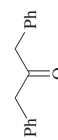

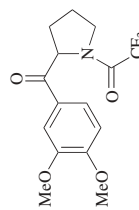
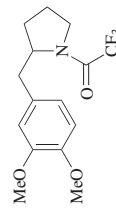
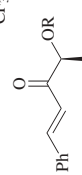
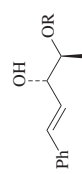
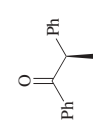
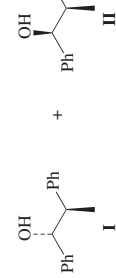
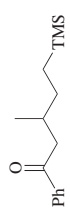

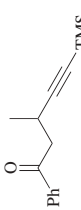
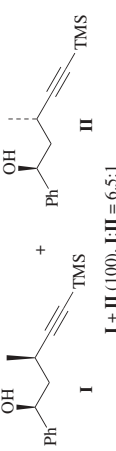
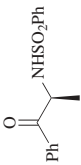

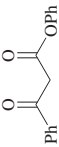
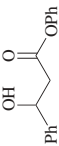
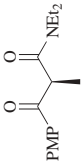

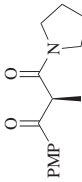

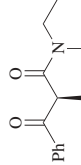

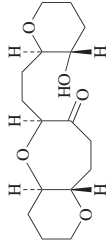
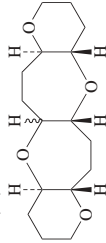
	Et_3SiH , TFA, CH_2Cl_2	 (96)	415
	Et_3SiH (2.6 eq), PPHF, TFA, 0° , 10 min, rt, 3 h	 (98)	135
	PMHS (3 eq), $(\text{C}_6\text{F}_5)_3\text{B}$ (5 mol%), CH_2Cl_2 , rt, 5-20 min	 (88)	354
	Et_3SiH (4 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (20 eq), reflux, 2 h, rt, 16 h	 (88)	376
	PhMe_2SiH (1.2 eq), TBAF (5-10 mol%), HMPA, 0°		86
	PhMe_2SiH (1.1-1.2 eq), TASF (5-10 mol%), HMPA	 I + II (90), I:II = 93:7	320
	Et_3SiH , $(\text{C}_6\text{F}_5)_3\text{B}$ (2 mol%), MeC_6H_5 , 0° , 1 h	 I + II (100), I:II = 1:1	372
	Et_3SiH , $(\text{C}_6\text{F}_5)_3\text{B}$ (2 mol%), MeC_6H_5 , 0° , 1 h	 I + II (100), I:II = 6.5:1	372

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 	PhMe ₂ SiH (1.1-1.2 eq), TFA, 0°, 20 h	 (66) threo:erythro = 2:98	86
	Ph ₂ SiH ₂ (1.2 eq), AlCl ₃ (1 eq), CH ₂ Cl ₂ , 20°, 24 h	 (77) + Ph ₂ SiHCl (—)	373
	PhMe ₂ SiH (1.2 eq), TASF (10 mol%), DMPU, 0°, 16 h	 I + II (92), I:II > 99:1	87
	PhMe ₂ SiH (1.2 eq), TASF (10 mol%), DMPU, 0°, 16 h	 I + II (92), I:II = 99:1	320
	PhMe ₂ SiH (1.2 eq), TFA, 0°, 5 h	 I + II (92), I:II = 99:1	87, 320
	PhMe ₂ SiH (1.2 eq), TASF, 0°	I + II (90), I:II = 99:1	87, 276
	Et ₃ SiH (1.1 eq), TFA, 0°, 4 h	II (90)	375
C ₁₆ 	Et ₃ SiH (10 eq), TMSOTf (1 eq), CH ₂ Cl ₂ , 0°, 10 min	 (75) trans:cis = 3:1	336
	Ph ₂ MeSiH (10 eq), TMSOTf (1 eq), CH ₂ Cl ₂ , 0°, 10 min	I (88) trans:cis 4:1	336

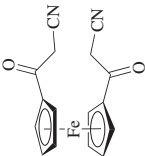

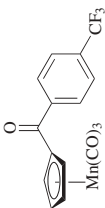
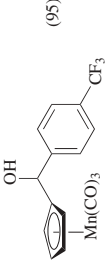

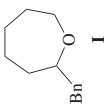
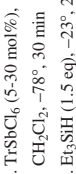

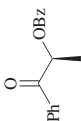
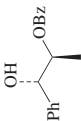

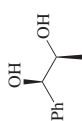
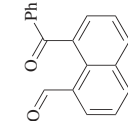
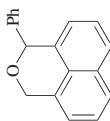
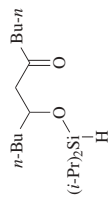
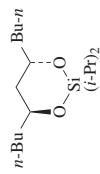
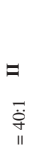
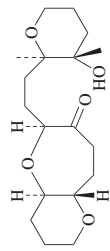
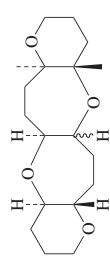
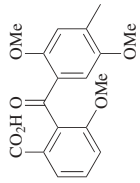
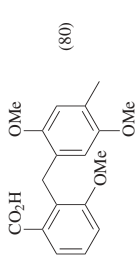
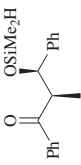
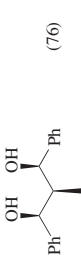
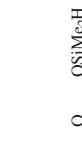

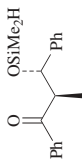
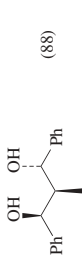

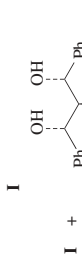
	 (41)	<p>Et₃SiH (6 eq), TFA, rt, 5 h</p>	179
	 (95)	<p>Et₃SiH, TFA, CHCl₃, 50-60°, 15 h</p>	351
	 (80)	<p>1. SbCl₅, TMSCl, SnI₂, CH₂Cl₂, -78°, 30 min 2. Et₃SiH (1.5 eq), -23°, 2.5 h</p>	306
	 I (95)	<p>1. TrSbCl₆ (5-30 mol %), CH₂Cl₂, -78°, 30 min 2. Et₃SiH (1.5 eq), -23°, 2.5 h</p>	306
	 (82) threoerythro = 96:4	<p>PhMe₂SiH (1.2 eq), TBAF (5-10 mol %), HMPA, 0°, 12 h</p>	86
	 (72) threoerythro = 7:93	<p>PhMe₂SiH (1.2 eq), TFA, 0°, 6 h</p>	86
 C ₁₇	 (98)	<p>Et₃SiH (8 eq), TMSOTf (1 eq), CH₂Cl₂, rt, 45 min</p>	339

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₇</p> 	SnCl ₄ (0.1 eq), -80°, 2 h	  I + II (60), I:II = 40:1	399
<p>C₁₈</p> 	Ph ₂ MeSiH (2 eq), TMSOTf (1 eq), CH ₂ Cl ₂ , 0°, 2 h	 (81) trans:cis = 3:1	336
	Et ₃ SiH, TFA		417
	TBAF (6 mol%), THF, -78°, 3.5 h		400
	BnOSiMe ₂ H, TBAF (6 mol%), THF, -78°, 3.5 h		400
	TBAF (6 mol%), THF, -78°, 3.5 h		400
	BnOSiMe ₂ H, TBAF (6 mol%), THF, -78°, 3.5 h		400

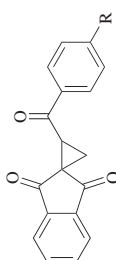
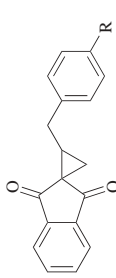
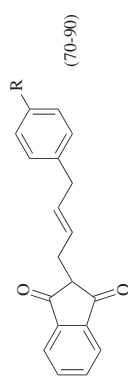
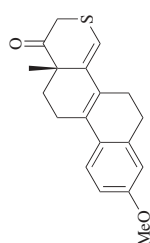
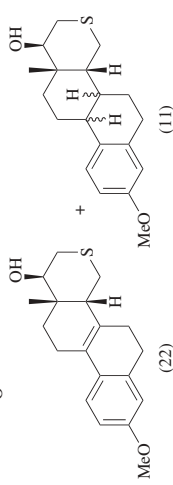
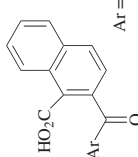
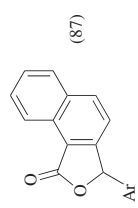
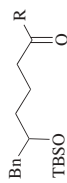
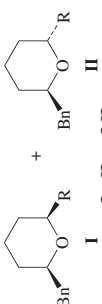
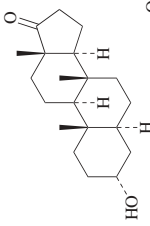
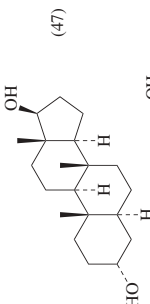
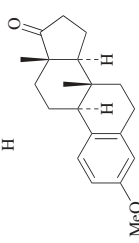
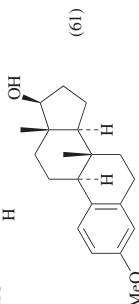
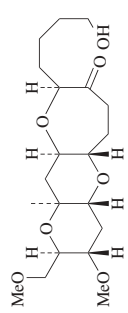
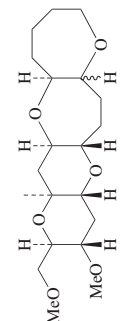
C ₁₈₋₁₉		Et ₃ SiH (8 eq), TFA (10 eq), 50°, 6 h		<table><tr><th>R</th><th>Time</th></tr><tr><td>F</td><td>24 h (57)</td></tr><tr><td>Cl</td><td>6 h (78)</td></tr><tr><td>Br</td><td>6 h (62)</td></tr><tr><td>OMe</td><td>2 h (57)</td></tr></table>	R	Time	F	24 h (57)	Cl	6 h (78)	Br	6 h (62)	OMe	2 h (57)	418						
R	Time																				
F	24 h (57)																				
Cl	6 h (78)																				
Br	6 h (62)																				
OMe	2 h (57)																				
C ₁₈₋₂₂	R = H, Et, <i>n</i> -Bu	Et ₃ SiH (3 eq), TFA (5 eq), 50°, 6 h	I (70-90)		755																
C ₁₈₋₂₃	<table><tr><th>R</th><th></th></tr><tr><td>H</td><td>I (81)</td></tr><tr><td>Me</td><td>(76)</td></tr><tr><td>Et</td><td>(78)</td></tr><tr><td><i>n</i>-Pr</td><td>(78)</td></tr><tr><td><i>i</i>-Pr</td><td>(74)</td></tr><tr><td><i>n</i>-Bu</td><td>(58)</td></tr><tr><td><i>n</i>-C₅H₁₁</td><td>(67)</td></tr></table>	R		H	I (81)	Me	(76)	Et	(78)	<i>n</i> -Pr	(78)	<i>i</i> -Pr	(74)	<i>n</i> -Bu	(58)	<i>n</i> -C ₅ H ₁₁	(67)	Et ₃ SiH (8 eq), TFA (10 eq), CH ₂ Cl ₂ , 0°, 30 min	I		756
R																					
H	I (81)																				
Me	(76)																				
Et	(78)																				
<i>n</i> -Pr	(78)																				
<i>i</i> -Pr	(74)																				
<i>n</i> -Bu	(58)																				
<i>n</i> -C ₅ H ₁₁	(67)																				
C ₁₉₋₂₃	R = Me, <i>n</i> -Pr, <i>n</i> -C ₅ H ₁₁	Et ₃ SiH (3 eq), TFA (5 eq), 6 h		(70-90)	755																
C ₁₉		Et ₃ SiH (2.5 eq), TFA, CH ₂ Cl ₂ , rt, 40 h		(22) + (11)	696																
	 Ar = 3-CF ₃ -C ₆ H ₄	Et ₃ SiH (5.1 eq), TFA, rt, 48 h		(87)	402																

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C_{19,26}</p> 	Et ₃ SiH (1.2 eq), BiBr ₃ (5 mol %), MeCN, rt		342
<p>R</p> <p>Me</p> <p><i>i</i>-Pr</p> <p>HOCH₂</p> <p>H₂C=CHCH₂</p> <p>EtO₂CCH₂</p> <p>Br(CH₂)₆</p> <p>Ph</p> <p>BzOCH₂</p> <p>BnOCH₂</p>		<p>I + II</p> <p>I:II</p> <p>(90) >99:1</p> <p>(95) >99:1</p> <p>(82) >99:1</p> <p>(95) >99:1</p> <p>(97) >99:1</p> <p>(96) >99:1</p> <p>(97) >99:1</p> <p>(93) >99:1</p> <p>(91) >99:1</p>	
<p>C₂₀</p> 	PhSiH ₃ (0.4 eq), Mn(dpm) ₃ (3 mol %), <i>i</i> -PrOH, DCE, O ₂ , rt	 <p>(47)</p>	367
	PhSiH ₃ (0.4 eq), Mn(dpm) ₃ (3 mol %), <i>i</i> -PrOH, DCE, O ₂ , rt	 <p>(61)</p>	367
	Ph ₃ MeSiH (2 eq), TMSOTf (1 eq), CH ₂ Cl ₂ , 0°, 2 h	 <p>(75) trans:cis = 3:1</p>	336

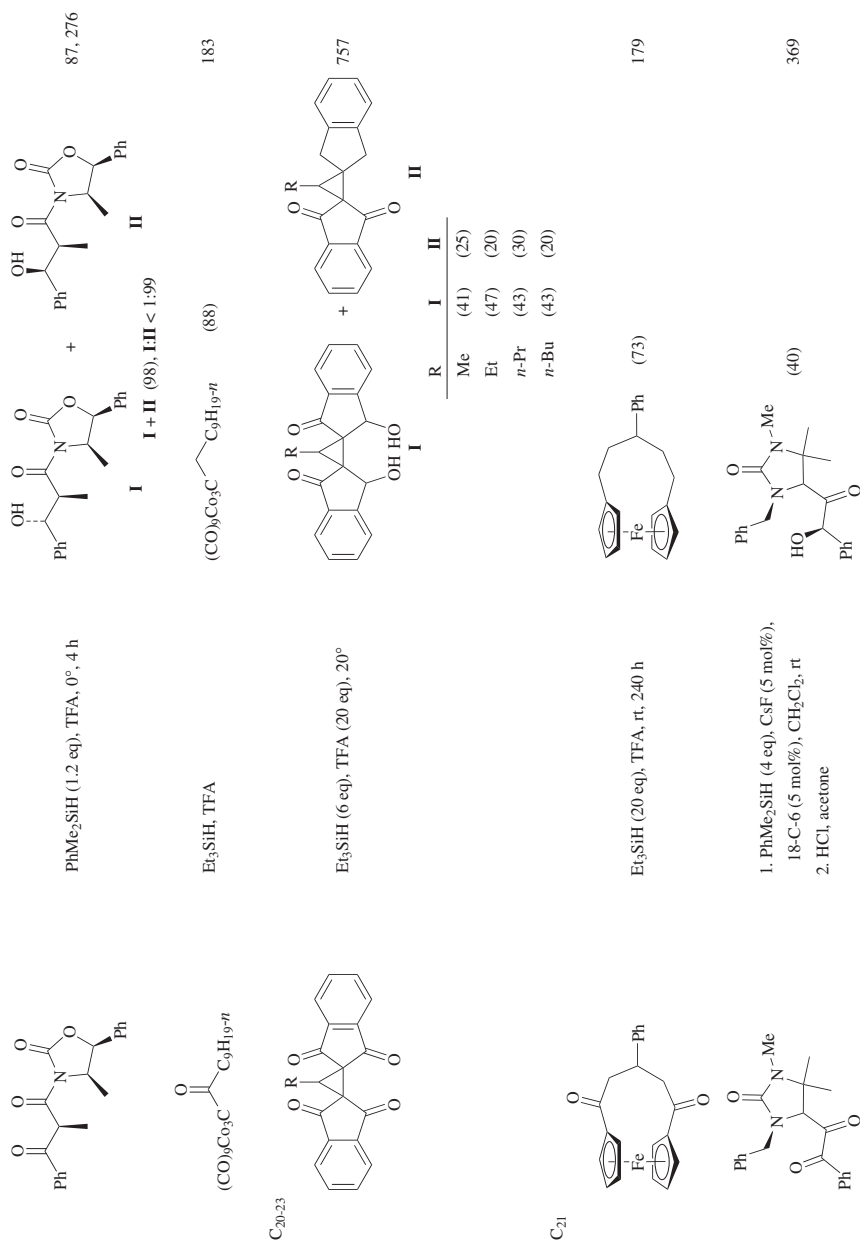
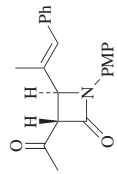
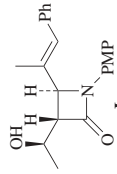
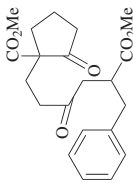
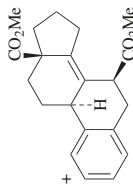
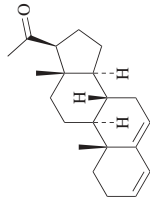
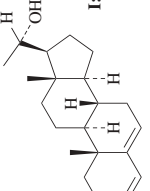
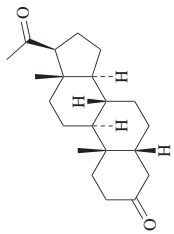
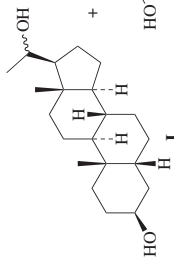


TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₁	PhMe ₂ SiH, TASF, THF, rt, 70 h	 I + II (50), I:II = 1:4	371
	PhMe ₂ SiH, TASF, THF, HMPA, rt, 23 h	I + II (90), I:II = 1:8	371
	PhMe ₂ SiH, TFA, THF, 0°, 22 h	I + II (90), I:II = 1:1	371
 (17)	Et ₃ SiH, TFA, CH ₂ Cl ₂ , rt, 16 h	 (18)	758
	1. TFA, 2 h 2. Et ₃ SiH, CH ₂ Cl ₂	I (25)	758
 I	Ph ₂ SiH ₂ , Rh-(+)-diop, C ₆ H ₆ , 22°	 II	573
	Ph ₂ SiH ₂ , Rh-(-)-diop, C ₆ H ₆ , 22°	I:II = 7:3	573
 II	Ph ₂ SiH ₂ , Rh-(+)-diop, C ₆ H ₆ , 22°	 I	573
	Ph ₂ SiH ₂ , Rh-(-)-diop, C ₆ H ₆ , 22°	I + II (—), I:II = 67:33	573
	Ph ₂ SiH ₂ , Rh-(+)-diop, C ₆ H ₆ , 22°	I + II (—), I:II = 64:36	573

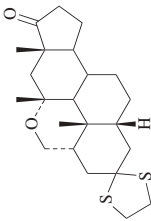
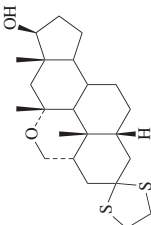
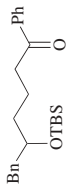
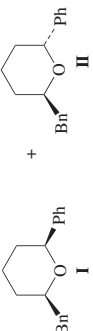
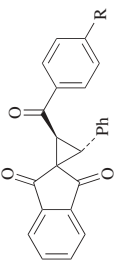
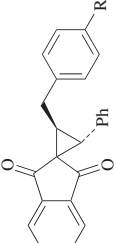
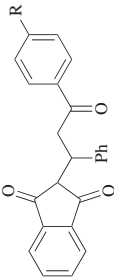
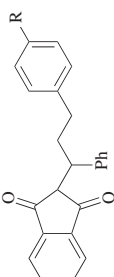
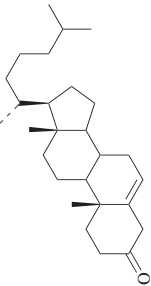
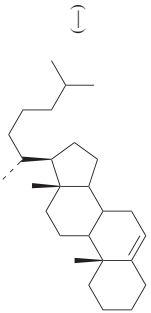
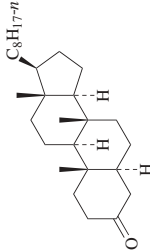
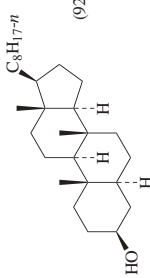
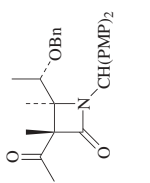
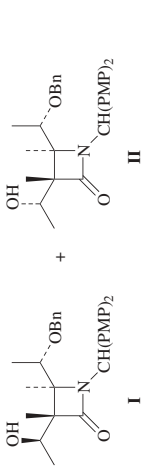
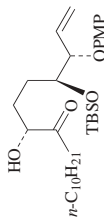
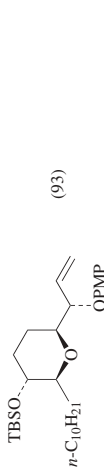
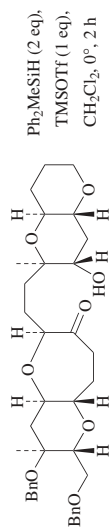
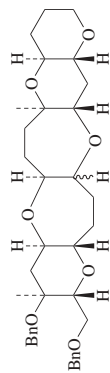
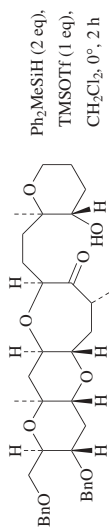
C ₂₃		1. Et ₃ SiH (10 eq), TFA (50 eq), CH ₂ Cl ₂ , 50°, 20 h 2. KOH, MeOH, THF, rt		368								
C ₂₄		Et ₃ SiH (1.2 eq), BiBr ₃ (5 mol%), MeCN, rt		342								
		Et ₃ SiH (1.2 eq), TMSBr (15 mol%), MeCN, rt	I + II (97) I:II > 99:1	342								
		Et ₃ SiH (1.2 eq), HBr (15 mol%), MeCN, rt	I + II (99), I:II > 99:1	342								
C ₂₄₋₂₆		Et ₃ SiH (6 eq), TFA (20 eq), 50°, 6 h		757								
		Et ₃ SiH (5 eq), TFA (10 eq), CCl ₄ , 50-55°, 8 h		266								
			<table><tr><th>R</th><th></th></tr><tr><td>H</td><td>(33)</td></tr><tr><td>Me</td><td>(49)</td></tr><tr><td>Et</td><td>(30)</td></tr></table>	R		H	(33)	Me	(49)	Et	(30)	
R												
H	(33)											
Me	(49)											
Et	(30)											

TABLE 12. ORGANOSILANE REDUCTION OF KETONES (Continued)

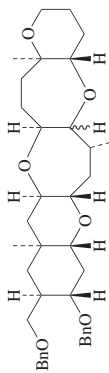
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₇	PMHS (3 eq), (C ₆ F ₅) ₃ B (5 mol%), CH ₂ Cl ₂ , rt, 5-20 min	 (–)	354
 C ₂₈	PhSiH ₃ (0.4 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE, O ₂ , rt	 (92)	367
 C ₃₁	Et ₃ SiH (3 eq), TFA (4 eq), BF ₃ ·OEt ₂ (0.23 eq), MeOC ₆ H ₅ , –25°, 1.5 h	 I + II	395
 C ₃₁	1. <i>t</i> -BuMe ₂ SiH, BiBr ₃ , MeCN, 0° 2. TBSOTf, 2,6-lutidine, 0°	 III + IV	404

C₃₇

336

C₃₈

336



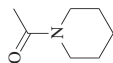
(55) trans:cis = 3:1

(62) trans:cis = 6:1

^a The yield was determined by NMR spectroscopy.^b The yield was determined by gas chromatography.^c This column gives the amount of acid used in a one mmol reaction.

TABLE 13. ORGANOSILANE REDUCTION OF AMIDES

Amide	Conditions			Product(s) and Yield(s) (%)	Refs.		
<div>$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{N}-\text{R}^2 \\ \\ \text{R}^3 \end{array}$</div>	<div>$\begin{array}{c} \text{R}^1-\text{CH}_2-\text{N}-\text{R}^2 \\ \\ \text{R}^3 \end{array}$</div>						
C ₅₋₁₃	Et ₃ SiH (3-3.5 eq), cat-1 (1 mol%), cat-2 (5 mol%), cat-3 (5 mol%), MeC ₆ H ₅ , 100°			432			
<div>$\begin{array}{c} \text{R}^1 \\ \text{H} \\ \text{H} \\ \text{H} \\ -(\text{CH}_2)_3- \\ -(\text{CH}_2)_4- \\ \text{Me} \\ -(\text{CH}_2)_5- \\ -(\text{CH}_2)_6- \\ 4\text{-MeC}_6\text{H}_4 \\ \text{Ph} \\ n\text{-C}_7\text{H}_{15} \\ \text{Me} \\ \text{Ph} \\ \text{H} \end{array}$</div>	<div>$\begin{array}{c} \text{R}^2 \\ -(\text{CH}_2)_4- \\ -(\text{CH}_2)_5- \\ -(\text{CH}_2)_5\text{O}(\text{CH}_2)_2- \\ \text{Me} \\ \text{Me} \\ -(\text{CH}_2)_2\text{O}(\text{CH}_2)_2- \\ \text{Me} \\ \text{H} \\ \text{H} \\ \text{Me} \\ \text{H} \\ \text{H} \\ \text{Bn} \\ \text{Me} \\ \text{Ph} \end{array}$</div>	<div>$\begin{array}{c} \text{R}^3 \\ \text{none} \\ \text{none} \\ \text{none} \\ \text{Me} \\ \text{Me} \\ \text{none} \\ \text{Me} \\ \text{H} \\ \text{H} \\ \text{Me} \\ \text{H} \\ \text{H} \\ \text{Bn} \\ \text{Me} \\ \text{Ph} \end{array}$</div>	<div>$\begin{array}{c} \text{Cat-1} \\ (\text{Ph}_3\text{P})_2\text{RuCl}_2(\text{CO})_2 \\ (\text{Ph}_3\text{P})_2\text{RuCl}_2(\text{CO})_2 \\ (\text{Ph}_3\text{P})_2\text{RuCl}_2(\text{CO})_2 \\ \text{Ru}_3(\text{CO})_{12} \\ \text{Ru}_3(\text{CO})_{12} \\ (\text{Ph}_3\text{P})_2\text{RuCl}_2(\text{CO})_2 \\ \text{Ru}_3(\text{CO})_{12} \\ \text{Ru}_3(\text{CO})_{12} \\ [\text{RuCl}_2(\text{CO})_3]_2 \\ [\text{RuCl}_2(\text{CO})_3]_2 \\ \text{Os}_3(\text{CO})_{12} \\ [\text{RuCl}_2(\text{CO})_3]_2 \\ \text{Os}_3(\text{CO})_{12} \\ \text{Ru}_3(\text{CO})_{12} \end{array}$</div>	<div>$\begin{array}{c} \text{Cat-2} \\ \text{EtI} \\ \text{EtI} \\ \text{EtI} \\ \text{none} \\ \text{none} \\ \text{EtI} \\ \text{none} \\ \text{none} \\ \text{EtI} \\ \text{Et}_2\text{NH} \\ \text{EtI} \\ \text{none} \\ \text{EtI} \\ \text{none} \\ \text{none} \end{array}$</div>	<div>$\begin{array}{c} \text{Cat-3} \\ \text{none} \\ \text{none} \\ \text{none} \\ \text{none} \\ \text{none} \\ \text{none} \\ \text{none} \\ \text{none} \\ \text{Et}_2\text{NH} \\ \text{Et}_2\text{NH} \\ \text{Et}_2\text{NH} \\ \text{Et}_2\text{NH} \\ \text{Et}_2\text{NH} \\ \text{none} \end{array}$</div>	<div>$\begin{array}{c} (92.9) \\ (86.1) \\ (87.0) \\ (87.7) \\ (86.6) \\ (92.3) \\ (99.2) \\ (95.9) \\ (50.3) \\ (97.1) \\ (56.0) \\ (99.5) \\ (99.5) \\ (93.2) \end{array}$</div>	
C ₅	<div>$\begin{array}{c} \text{O} \\ \parallel \\ t\text{-BuO}-\text{C}-\text{NH}_2 \end{array}$</div>	<div>$\begin{array}{c} \text{O} \\ \parallel \\ t\text{-BuO}-\text{C}-\text{NHBn} \end{array}$</div>			326		
Et ₃ SiH (3 eq), TFA (2-3 eq), PhCHO (x eq), MeCN, 22°, 18 h							
<div>$\frac{\text{x}}{0.33}$ 3</div>							
<div>$\begin{array}{c} (92) \\ (81) \end{array}$</div>							



Et₃SiH (3-3.5 eq), cat-1 (1 mol%),
cat-2 (5 mol%), cat-3 (5 mol%),
MeC₆H₅, 100°

I


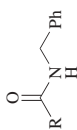




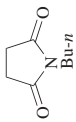

Cat-1	Cat-2	Cat-3	Time
Mn ₂ (CO) ₁₀	none	Et ₂ NH	16 h (89.3)
Re ₂ (CO) ₁₀	none	Et ₂ NH	16 h (95.6)
Ru ₃ (CO) ₁₂	none	none	16 h (88.2)
(Ph ₃ P) ₂ RuCl ₂ (CO) ₂	EtI	none	16 h (96.1)
(Ph ₃ P) ₂ RuCl ₂ (CO) ₂	MeI	none	16 h (98.1)
(Ph ₃ P) ₂ RuCl ₂ (CO) ₂	I ₂	none	16 h (94.1)
(Ph ₃ P) ₃ RuH ₂ (CO)	EtI	Et ₂ NH	40 h (94.4)
Ru(acac) ₃	EtI	Et ₂ NH	16 h (88.0)
Os ₃ (CO) ₁₂	none	Et ₂ NH	16 h (99.8)
Os ₃ (CO) ₁₂	none	pyridine	16 h (99.3)
(Ph ₃ P) ₄ RhH	none	Et ₂ NH	16 h (99.5)
IrCl ₃	none	none	16 h (94.4)
K ₂ IrCl ₆	none	Et ₂ NH	16 h (92.6)
Pd(OH) ₂ /C	none	Et ₂ NH	40 h (77.7)
PtCl ₂	none	Et ₂ NH	16 h (78.5)

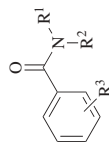
R₃SiH (3-3.5 eq), cat-1 (1 mol%),
cat-2 (5 mol%), cat-3 (5 mol%),
MeC₆H₅, 100°

I

R ₃ Si	Cat-1	Cat-2	Cat-3	Time	I
PhMe ₂ Si	(Ph ₃ P) ₂ RuCl ₂ (CO) ₂	EtI	none	16 h	(90.2)
<i>i</i> -BuMe ₂ Si	(Ph ₃ P) ₂ RuCl ₂ (CO) ₂	EtI	none	16 h	(70.4)
<i>i</i> -Pr ₃ Si	[RuCl ₂ (CO) ₃] ₂	EtI	Et ₂ NH	40 h	(50.6)
ClMe ₂ Si	Os ₃ (CO) ₁₂	none	Et ₂ NH	16 h	(80.1)
Me ₂ (EtO)Si	(Ph ₃ P) ₂ RuCl ₂ (CO) ₂	EtI	none	16 h	(93.1)
Me(EtO) ₂ Si	(Ph ₃ P) ₂ RuCl ₂ (CO) ₂	EtI	none	16 h	(90.8)
(EtO) ₃ Si	[RuCl ₂ (CO) ₃] ₂	EtI	Et ₂ NH	16 h	(86.1)

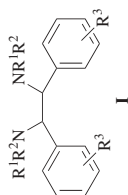
TABLE 13. ORGANOSILANE REDUCTION OF AMIDES (Continued)

Amide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 	Et_3SiH (3 eq), TFA (2-3 eq), PhCHO (x eq)		326
R	Solvent	Temp	Time
Ph	MeC ₆ H ₅	120°	18 h
4-FC ₆ H ₄	MeC ₆ H ₅	120°	18 h
PhO	MeCN	22°	18 h
PhNH	MeC ₆ H ₅	22°	18 h
Bn	MeC ₆ H ₅	120°	36 h
4-MeOC ₆ H ₄	MeC ₆ H ₅	120°	18 h
BnO	MeCN	22°	18 h
BnNH	MeC ₆ H ₅	22°	18 h
		x = 0.33	x = 3
		(91)	(94)
		(92)	(93)
		(90)	(85)
		(92)	(97)
		(92)	(68)
		(95)	(91)
		(95)	(92)
		(89)	(88)
C_7 	Et_3SiH (3 eq), TFA (2.9 eq), EtCH(OEt) ₂ (0.33 eq), MeCN, 22°, 18 h		326
C_8 	Ph_2SiH_2 (2.1 eq), (Ph ₃ P) ₃ Rh(CO) (0.1 mol%), THF, rt, 0.5 h		431
	Ph_2SiH_2 (4.3 eq), (Ph ₃ P) ₃ Rh(CO) (1 mol%), THF, rt, 3.5 h		431



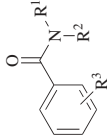
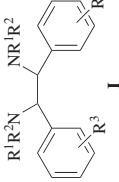

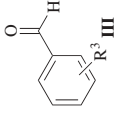
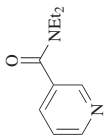
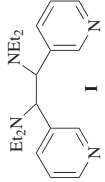
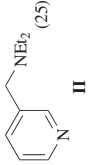
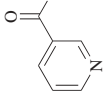
PhMeSiH₂ (2 eq), catalyst (1 mol%),
MeC₆H₅, 80°, 1 h

R ¹	R ²	R ³
Me	Me	H
Me	Me	H
Et	Et	H
Et	Et	H
Et	Et	4-Cl
Et	Et	4-Cl
Et	Et	4-Me
Et	Et	4-CF ₃
Et	Et	4-MeO
Me	Ph	H



	meso:rac
(84)	52:48
(80)	52:48
(92)	52:48
(88)	53:47
(93)	53:47
(90)	53:47
(91)	62:38
(96)	53:47
(94)	56:44
(77)	50:50

TABLE 13. ORGANOSILANE REDUCTION OF AMIDES (Continued)

Amide	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C_{9,14}</p> 	<p>1. PhMeSiH₂ (3 mmol), Cp₂TiF₂ (0.1 mol), MeC₆H₅, 70°, 10 min</p> <p>2. PhMeSiH₂ (2 mmol), amide (1 mmol), MeC₆H₅, 20°, 30 min</p>	<p> I</p> <p>+  II</p> <p>+  III</p>	430
<p>C₁₀</p> 	<p>PhMeSiH₂ (2 eq), Cp₂TiF₂ (1 mol%), MeC₆H₅, 80°, 1 h</p>	<p> I</p> <p>+  II</p> <p>(27) meso:rac = 57:43</p>	430
	<p>1. PhMeSiH₂ (3 mmol), Cp₂TiF₂ (0.1 mol), MeC₆H₅, 70°, 10 min</p> <p>2. PhMeSiH₂ (2 mmol), amide (1 mmol), MeC₆H₅, 20°, 30 min</p>	<p>I (43.5) meso:rac = 56:44 + II (34.1) +  III (22.4)</p>	430

R ¹	R ²	R ³
Me	Me	H
Et	Et	H
Et	Et	4-Cl
Et	Et	4-MeO
Et	Et	4-Me
Et	Et	4-CF ₃
Me	Ph	H

C₁₀₋₁₉


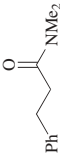

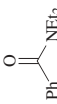
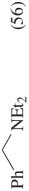

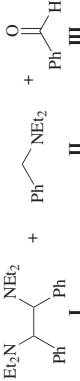


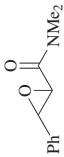

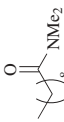

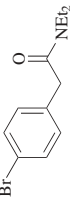
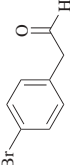


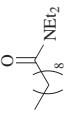

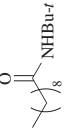

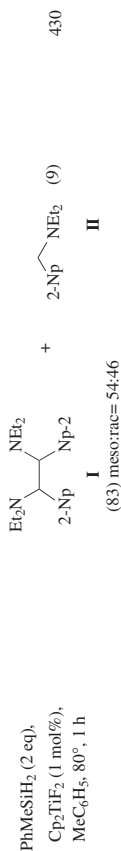
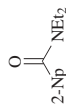
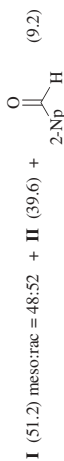
C ₁₀₋₁₉		Ph_3SiH_2 (2.1 eq), (Ph ₃ P) ₃ RhH(CO) (0.1 mol%), THF, rt	$\text{R}^1\text{---NR}_2$	431																																						
	R ¹	Time																																								
	MeO ₂ CCH ₂ CH ₂	N(CH ₂) ₅	(98)																																							
	Ph	NEt ₂	(85)																																							
	4-BrC ₆ H ₄	NEt ₂	(85)																																							
	<i>i</i> -Pr	NBu ₂	(90)																																							
	<i>t</i> -Bu	NBu ₂	(86)																																							
	4-MeO ₂ CC ₆ H ₄	NEt ₂	(70)																																							
	Ph	NMe(C ₆ H ₁₁ - <i>c</i>)	(91)																																							
	Ph	N(C ₆ H ₁₁ - <i>O</i>) ₂	(83)																																							
C ₁₁		1. EtMe ₂ SiH (2.5 eq), 2 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add acid, 0.5 h		(75)	280																																					
		1. EtMe ₂ SiH (2.5 eq), 2 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Acid, 0.5 h		(56)	280																																					
		Silane (1 eq), Cp ₂ TF ₂ (0.1 mol), MeC ₆ H ₅ , 1 h	 I II III																																							
		<table> <tr> <th>Silane</th><th>Temp</th></tr> <tr> <td>PhSiH₃</td><td>20°</td></tr> <tr> <td>PhSiH₃</td><td>80°</td></tr> <tr> <td><i>n</i>-C₆H₁₃SiH₃</td><td>20°</td></tr> <tr> <td><i>n</i>-C₆H₁₃SiH₃</td><td>80°</td></tr> <tr> <td>[—(Me)(H)SiO—]₄</td><td>20°</td></tr> <tr> <td>[—(Me)(H)SiO—]₄</td><td>80°</td></tr> <tr> <td>PMHS</td><td>20°</td></tr> <tr> <td>PMHS</td><td>80°</td></tr> </table>	Silane	Temp	PhSiH ₃	20°	PhSiH ₃	80°	<i>n</i> -C ₆ H ₁₃ SiH ₃	20°	<i>n</i> -C ₆ H ₁₃ SiH ₃	80°	[—(Me)(H)SiO—] ₄	20°	[—(Me)(H)SiO—] ₄	80°	PMHS	20°	PMHS	80°	<table> <tr> <th>I:II:III</th><th>I mesorac</th></tr> <tr> <td>92:8:0</td><td>54:46</td></tr> <tr> <td>100:0:0</td><td>57:43</td></tr> <tr> <td>51:30:19</td><td>55:45</td></tr> <tr> <td>85:15:0</td><td>56:44</td></tr> <tr> <td>43:9:48</td><td>52:48</td></tr> <tr> <td>92:8:0</td><td>55:45</td></tr> <tr> <td>59:1:49</td><td>56:44</td></tr> <tr> <td>(—)</td><td>(—)</td></tr> <tr> <td>(—)</td><td>(0)</td></tr> </table>	I:II:III	I mesorac	92:8:0	54:46	100:0:0	57:43	51:30:19	55:45	85:15:0	56:44	43:9:48	52:48	92:8:0	55:45	59:1:49	56:44	(—)	(—)	(—)	(0)	
Silane	Temp																																									
PhSiH ₃	20°																																									
PhSiH ₃	80°																																									
<i>n</i> -C ₆ H ₁₃ SiH ₃	20°																																									
<i>n</i> -C ₆ H ₁₃ SiH ₃	80°																																									
[—(Me)(H)SiO—] ₄	20°																																									
[—(Me)(H)SiO—] ₄	80°																																									
PMHS	20°																																									
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I:II:III	I mesorac																																									
92:8:0	54:46																																									
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59:1:49	56:44																																									
(—)	(—)																																									
(—)	(0)																																									

TABLE 13. ORGANOSILANE REDUCTION OF AMIDES (Continued)

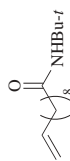
Amide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁			
	1. EtMe ₂ SiH (2.5 eq), 225 (1 mol%), 1,4-dioxane, 20°, 0.5 h 2. Add acid, 2 h	 (45)	280
	Ph ₂ SiH ₂ (2.1 eq), (Ph ₃ P) ₃ Rh(CO) (0.1 mol%), THF, rt, 3 h	 (65)	431
C ₁₂			
	Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°	 (74)	433
	Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°	 (80)	433
	Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°	 (65)	433
C ₁₄			
	Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°	 (90)	433
	Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°	 I (90)	433

C₁₅

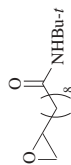
430



430



433



433

C₁₆

431

R ₃ Si	Catalyst	Time
Ph ₂ HSi	(Ph ₃ P) ₃ RhH(CO)	1 h (94)
Ph ₂ HSi	(Ph ₃ P) ₄ RhH	0.5 h (93)
Ph ₂ HSi	[Rh(cod) ₂]BF ₄	42 h (86)
Ph ₂ HSi	(Ph ₃ P) ₃ RhCl	48 h (93)
Ph ₂ HSi	RhCl ₃ •3H ₂ O	48 h (95)
Ph ₃ Si	(Ph ₃ P) ₃ RhH(CO)	— (0)

TABLE 13. ORGANOSILANE REDUCTION OF AMIDES (Continued)

	Amide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₆		Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°		433
		Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°		433
C ₁₇		Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°		433
		Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°		433
C ₁₈		Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°		433
		Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°		433
C ₂₀		Ph ₂ SiH ₂ (1.1 eq), Ti(OPr- <i>i</i>) ₄ (1.0 eq), 20°		433

TABLE 14. ORGANOSILANE REDUCTIVE AMINATION OF ALDEHYDES AND KETONES

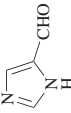
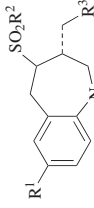


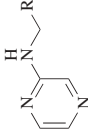
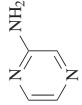
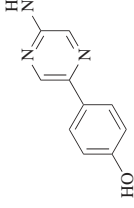
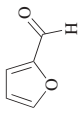
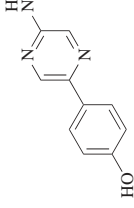
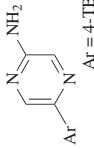
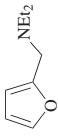



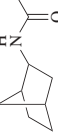








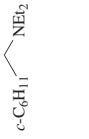




Aldehyde/Ketone	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄				360
		Et ₃ SiH (2 eq), TFA, CH ₂ Cl ₂ , rt		
			 (90)	
		Time		
		2 h	(90)	
		4 h	(94)	
		4 h	(93)	
		4 h	(95)	
		4 h	(93)	
		4 h	(90)	
C ₄₋₁₂		PhSiH ₃ (1.1 eq), (<i>n</i> -Bu) ₂ SnCl ₂ (0.02 eq), THF, 20° or reflux, 24-300 h		362
				
			R	
			<i>n</i> -Pr (63)	
			<i>i</i> -Pr (70)	
			Ph (72)	
			Bn (50)	
			<i>n</i> -C ₁₁ H ₂₃ (56)	
				
			R	
C ₅		PhSiH ₃ (1.1 eq), (<i>n</i> -Bu) ₂ SnCl ₂ (0.02 eq), THF, TBAF, 20° or reflux, 24-300 h		362
				
			Ar = 4-TBSOC ₆ H ₄	
			<i>n</i> -Pr (25)	
			<i>i</i> -Pr (41)	
			Ph (17)	
			Bn (10)	
			<i>n</i> -C ₁₁ H ₂₃ (57)	
			 (65)	
				359
C ₅		Me ₂ SiH(NEt ₂) (1.2 eq)		
		TiCl ₄ (0.20 eq), CH ₂ Cl ₂ , 0° to rt, 36 h		

TABLE 14. ORGANOSILANE REDUCTIVE AMINATION OF ALDEHYDES AND KETONES (Continued)

Aldehyde/Ketone	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	MeCN	Et ₃ SiH (1.1 eq), H ₂ SO ₄ , H ₂ O, 28°, 65 h	 (67)	313
C ₇ 	MeCN	Et ₃ SiH (1.1 eq), H ₂ SO ₄ , H ₂ O, 28°, 65 h	 (78)	313
	BaNH ₂	1. Ti(OPr- <i>i</i>) ₄ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 4.5 h	 (88)	363
	PhNH ₂	1. Ti(OPr- <i>i</i>) ₄ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 4.5 h	 (87)	363
		1. Ti(OPr- <i>i</i>) ₄ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 5 h	 (85)	363
	Me ₂ SiH(NEt ₂) (1.2 eq)	ZnI ₂ (0.10 eq), CH ₂ Cl ₂ , 0° to rt, 36 h	 (81)	359
	BaNH ₂	1. Ti(OPr- <i>i</i>) ₄ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 5 h	 (90)	363
	PhNH ₂	1. Ti(OPr- <i>i</i>) ₄ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 5 h	 (92)	363


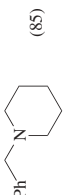
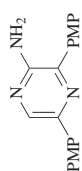
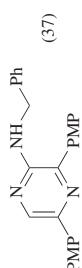
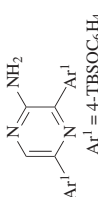
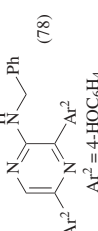

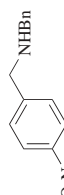
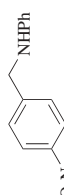
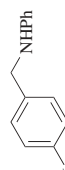
	1. $\text{Ti}(\text{OPr-}i)_4$ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 5.5 h		363								
	PhSiH_3 (1.1 eq), $(n\text{-Bu})_2\text{SnCl}_2$ (0.02 eq), THF, 20°, 24 h		362								
	PhSiH_3 (1.1 eq), $(n\text{-Bu})_2\text{SnCl}_2$ (0.02 eq), THF, TBAF, 20°, 24 h		362								
$\text{Ar}^1 = 4\text{-TBSOC}_6\text{H}_4$		$\text{Ar}^2 = 4\text{-HOC}_6\text{H}_4$									
PhNH_2	PhSiH_3 (1.1 eq), $(n\text{-Bu})_2\text{SnCl}_2$ (0.02 eq), THF, rt, 2-24 h		361								
BnNH_2	1. $\text{Ti}(\text{OPr-}i)_4$ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 4 h		363								
PhNH_2	PhSiH_3 (1.1 eq), $(n\text{-Bu})_2\text{SnCl}_2$ (0.02 eq), THF, rt, 2-24 h		361								
PhNH_2	PhSiH_3 (1.1 eq), $(n\text{-Bu})_2\text{SnCl}_2$ (0.02 eq), THF, rt, 2-24 h		361								
BnNH_2	1. MgSO_4 , CH_2Cl_2 , rt, 1 h 2. Cl_3SiH , $\text{CH}_2\text{Cl}_2/\text{DMF}$ (4:1), 0°, 4 h	<table><tr><th>R</th><th>R</th></tr><tr><td>$c\text{-C}_6\text{H}_{11}$</td><td>(74)</td></tr><tr><td>$(E)\text{-PhCH=CH}$</td><td>(81)</td></tr><tr><td>BnCH_2</td><td>(93)</td></tr></table>	R	R	$c\text{-C}_6\text{H}_{11}$	(74)	$(E)\text{-PhCH=CH}$	(81)	BnCH_2	(93)	318
R	R										
$c\text{-C}_6\text{H}_{11}$	(74)										
$(E)\text{-PhCH=CH}$	(81)										
BnCH_2	(93)										

TABLE 14. ORGANOSILANE REDUCTIVE AMINATION OF ALDEHYDES AND KETONES (Continued)

Aldehyde/Ketone	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.		
C_{7-10}						
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$	$\text{R}^3\text{R}^4\text{NSiHMe}_2$ (1.2 eq)	Catalyst (x eq), CH_2Cl_2 , 0° to rt	$\begin{array}{c} \text{NR}^3\text{R}^4 \\ \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$	359		
R^1	R^3	R^4	Catalyst	x	Time	
Ph	Me	Me	TiCl_4	0.2	36 h	(64)
Ph	Me	Me	TiCl_4	0.4	36 h	(73)
4-MeC ₆ H ₄	Me	Me	TiCl_4	0.2	36 h	(67)
4-MeC ₆ H ₄	Me	Me	TiCl_4	0.4	36 h	(85)
4-O ₂ NC ₆ H ₄	Me	Me	TiCl_4	0.2	48 h	(94)
Ph	Me	Me	TiCl_4	0.4	36 h	(87)
BnCH ₂	Me	Me	ZnI_2	0.1	36 h	(72)
BnCH ₂	Me	Me	TiCl_4	0.2	48 h	(67)
Ph	Me	Me	TiCl_4	0.3	36 h	(77)
BnCH ₂	Me	Me	ZnI_2	0.1	36 h	(71)
Ph	Me	Me	TiCl_4	0.2	36 h	(83)
BnCH ₂	Me	Me	ZnI_2	0.1	36 h	(66)
Ph	Me	Me	Ph_3CClO_4	0.05	2 h	(94)
Ph	Me	Me	Ph_3CClO_4	0.05	1 h	(53)
BnCH ₂	Me	Me	Ph_3CClO_4	0.05	3 h	(40)
BnCH ₂	Me	Me	Ph_3CClO_4	0.05	1 h	(88)
BnCH ₂	Me	Me	Ph_3CClO_4	0.05	1 h	(86)

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$	$\begin{array}{c} \text{R}^3\text{NH}_2 \end{array}$	1. Activator (1.25 eq), solvent, rt, 1 h 2. PMHS (2 eq), THF			$\begin{array}{c} \text{NHR}^3 \\ \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$
R ¹	R ²	R ³	Activator	Solvent	Time (2)
Ph	H	Bn	AlCl ₃	MeC ₆ H ₅	12 h (40)
Ph	H	Bn	Pd-C	EtOH	10 h (60)
Ph	H	Bn	Ti(OPr- <i>i</i>) ₄	THF	5 h (90)
Ph	H	Ph	AlCl ₃	MeC ₆ H ₅	12 h (52)
Ph	H	Ph	Pd-C	EtOH	10 h (62)
Ph	H	Ph	Ti(OPr- <i>i</i>) ₄	THF	5 h (92)
(<i>E</i>)-PhCH=CH	H	Bn	AlCl ₃	MeC ₆ H ₅	10 h (48)
(<i>E</i>)-PhCH=CH	H	Bn	Pd-C	EtOH	8 h (55)
(<i>E</i>)-PhCH=CH	H	Bn	Ti(OPr- <i>i</i>) ₄	THF	4 h (85)
(<i>E</i>)-PhCH=CH	H	Ph	AlCl ₃	MeC ₆ H ₅	12 h (45)
(<i>E</i>)-PhCH=CH	H	Ph	Pd-C	EtOH	9 h (56)
(<i>E</i>)-PhCH=CH	H	Ph	Ti(OPr- <i>i</i>) ₄	THF	4.5 h (88)
Ph	Me	Bn	AlCl ₃	MeC ₆ H ₅	13 h (45)
Ph	Me	Bn	Pd-C	EtOH	10 h (55)
Ph	Me	Bn	Ti(OPr- <i>i</i>) ₄	THF	6 h (90)
Ph	Me	Ph	AlCl ₃	MeC ₆ H ₅	13 h (50)
Ph	Me	Ph	Pd-C	EtOH	10 h (58)
Ph	Me	Ph	Ti(OPr- <i>i</i>) ₄	THF	6 h (90)

TABLE 14. ORGANOSILANE REDUCTIVE AMINATION OF ALDEHYDES AND KETONES (Continued)

Aldehyde/Ketone	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇₋₁₃				
$\begin{array}{c} \text{O} \\ \parallel \\ \text{Ar}-\text{C}-\text{R} \end{array}$	Me ₂ SiH(NEt ₂) (1.2 eq)	TiCl ₄ (0.20 eq), CH ₂ Cl ₂ , 0° to rt, 36 h	$\begin{array}{c} \text{NEt}_2 \\ \\ \text{Ar}-\text{C}-\text{R} \end{array}$	359
Ar	R			
Ph	H		(90)	
4-ClC ₆ H ₄	H		(78)	
4-O ₂ NC ₆ H ₄	H		(85)	
Ph	Me		(65)	
4-MeC ₆ H ₄	H		(91)	
4-MeOC ₆ H ₄	H		(92)	
4-NCC ₆ H ₄	H		(84)	
Ph	Et		(39)	
4-MeO ₂ CC ₆ H ₄	H		(84)	
Ph	Ph		(46)	
4-PhC ₆ H ₄	H		(86)	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{R}^2 \end{array}$	MeCN	Et ₃ SiH (1.1 eq), H ₂ SO ₄ , H ₂ O, 28°	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C}-\text{N}-\text{H} \\ \\ \text{R}^2 \end{array}$	313
R ¹	R ²	Time		
—(CH ₂) ₅ —		72 h	(30)	
Ph	H	74 h	(80)	
Ph	Me	72 h	(85)	
n-C ₇ H ₁₅	H	72 h	(0)	
Ph	Ph	48 h	(63)	




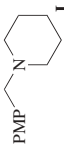

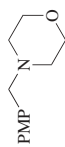
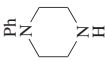
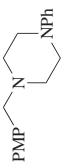



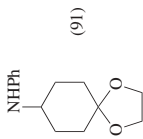
C_{7,23}

$\begin{array}{c} \text{O} \\ \parallel \\ \text{Ar}-\text{C}-\text{H} \end{array}$	PhCONH ₂ (3 eq)	Et ₃ SiH (3 eq), TFA (2.9 eq), MeC ₆ H ₅ , 120°, 18 h	Ar-CH ₂ -NHCOPh	326
Ar				
4-FC ₆ H ₄			(96)	
4-MeO ₂ CC ₆ H ₄			(91)	
4-HO ₂ CC ₆ H ₄			(96)	
4-AcOC ₆ H ₄			(75)	
4-BnOC ₆ H ₄			(90)	
4-TBSOC ₆ H ₄			(46)	
4-TBDPSOC ₆ H ₄			(91)	

C₈

$\begin{array}{c} \text{O} \\ \parallel \\ \text{PMP}-\text{C}-\text{H} \end{array}$	PhNH ₂	R ₃ SiH (x eq), (<i>n</i> -Bu) ₂ SnCl ₂ (0.02 eq), PhNH ₂ (1.0 eq), THF, rt, 21 h	$\begin{array}{c} \text{PMP}-\text{CH}_2-\text{N}-\text{Ph} \\ \\ \text{H} \end{array}$	361
		R ₃ Si		
		Et ₃ Si	(0)	
		Ph ₃ Si	(0)	
		Ph ₂ HSi	(88)	
		Ph ₂ HSi	(—)	
		PhH ₂ Si	(82)	
		PhH ₂ Si	(83)	
		PhH ₂ Si	(83)	
		PhH ₂ Si	(83)	
		PhH ₂ Si	(—)	
		PMHS	(82)	
		PhH ₂ Si	(0)	
	NHMePh	PhSiH ₃ (1.1 eq), (<i>n</i> -Bu) ₂ SnCl ₂ (0.02 eq), THF, rt, 2-24 h	$\begin{array}{c} \text{PMP}-\text{CH}_2-\text{N}-\text{Ph} \\ \quad \\ \text{Me} \end{array}$	361

TABLE 14. ORGANOSILANE REDUCTIVE AMINATION OF ALDEHYDES AND KETONES (Continued)

Aldehyde/Ketone	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	$ArNH_2$	$PhSiH_3$ (1.1 eq), $(n-Bu)_2SnCl_2$ (0.02 eq), THF, rt, 2-24 h		361
	Ar		(82)	
	$4-MeOC_6H_4$		(85)	
	$4-O_2NC_6H_4$		(85)	
	$4-t-BuC_6H_4$			
		$PhSiH_3$ (1.1 eq), $(n-Bu)_2SnCl_2$ (0.02 eq), THF, rt, 16 h	 (70)	361
		$PhSiH_3$ (1.1 eq), THF, rt, 16 h	I (13)	361
		$PhSiH_3$ (1.1 eq), $(n-Bu)_2SnCl_2$ (0.02 eq), THF, rt, 16 h	 (78)	361
		$PhSiH_3$ (1.1 eq), $(n-Bu)_2SnCl_2$ (0.02 eq), THF, rt, 16 h	 (67)	361
	Et_2NH	$PhSiH_3$ (1.1 eq), $(n-Bu)_2SnCl_2$ (0.02 eq), THF, rt, 16 h	 (49)	361
	$PhNH_2$	$PhSiH_3$ (1.1 eq), $(n-Bu)_2SnCl_2$ (0.02 eq), THF, rt, 2-24 h	 (85)	361
	$PhNH_2$	$PhSiH_3$ (1.1 eq), $(n-Bu)_2SnCl_2$ (0.1 eq), THF, rt, 2-24 h	 (91)	361



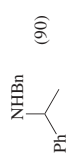

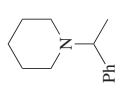

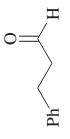
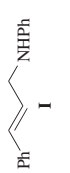
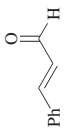



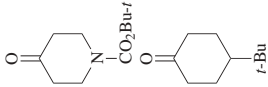
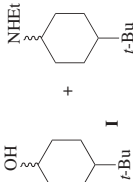
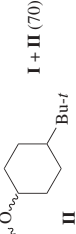

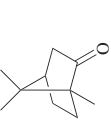
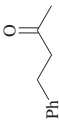



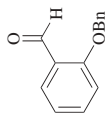
	PhNH_2	PhSiH_3 (1.1 eq), (<i>n</i> -Bu) $_2\text{SnCl}_2$ (0.1 eq), THF, rt, 2-24 h		361
	PhNH_2	1. $\text{Ti}(\text{OPr-}i)_4$ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 6 h	I (90)	363
	BuNH_2	1. $\text{Ti}(\text{OPr-}i)_4$ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 6 h		363
		1. $\text{Ti}(\text{OPr-}i)_4$ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 6 h		363
C_9	$\text{Me}_2\text{SiH}(\text{NEt}_2)$ (1.2 eq)	ZnI_2 (0.10 eq), CH_2Cl_2 , 0° to rt, 36 h		359
	PhNH_2	PhSiH_3 (1.1 eq), (<i>n</i> -Bu) $_2\text{SnCl}_2$ (0.02 eq), THF, rt, 2-24 h		361
		1. $\text{Ti}(\text{OPr-}i)_4$ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 4.5 h	I (88)	363
	BuNH_2	1. $\text{Ti}(\text{OPr-}i)_4$ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 4 h		363
		1. $\text{Ti}(\text{OPr-}i)_4$ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 4.5 h		363

TABLE 14. ORGANOSILANE REDUCTIVE AMINATION OF ALDEHYDES AND KETONES (Continued)

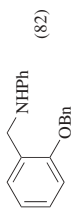
Aldehyde/Ketone	Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	PhNH ₂	PhSiH ₃ (1.1 eq), (<i>n</i> -Bu) ₂ SnCl ₂ (0.02 eq), THF, rt, 2-24 h	(86)	361
	MeCN	Et ₃ SiH (1.1 eq), H ₂ SO ₄ , H ₂ O, 28°, 65 h	(4) +  +  +  (21)	313
	BuNH ₂	1. Ti(OPr- <i>i</i>) ₄ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 4.5 h	(88)	363
	Me ₂ SiH(NEt ₂) (1.2 eq)	ZnI ₂ (0.10 eq), CH ₂ Cl ₂ , 0° to rt, 36 h	(46)	359
C ₁₃ 		1. Ti(OPr- <i>i</i>) ₄ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 4.5 h	(80)	363
	ArNH ₂	1. Ti(OPr- <i>i</i>) ₄ (1.25 eq), THF, rt, 1 h 2. PMHS (2 eq), THF, 4.5 h	NHAr  (85) (83)	363

C₁₄








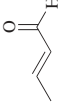
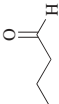
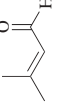
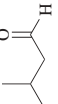
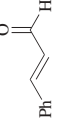
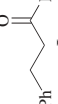




















PhNH₂

PhSiH₃ (1.1 eq),
n-Bu₂SnCl₂ (0.02 eq),
 THF, rt, 2-24 h



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TABLE 15. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ALDEHYDES

Unsaturated Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et ₃ SiH (3 eq), TFA (6 eq), CHCl ₃ , 40°, 6 h	 (10) +  (12) +  (9) +  + CF ₃ CO ₂ Pr- <i>n</i> (—)	434
	PhSiH ₃ (1.01 eq), Ni, PPh ₃ (0.02 eq)	 (100)	438
	PhSiH ₃ (1.01 eq), Ni, PPh ₃ (0.02 eq)	 (100)	438
	Ph ₂ SiH ₂ (2.3 eq), CsF (1 eq), rt, 3 min Et ₃ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl, C ₆ H ₆ , 45°, 1 h Ph ₂ SiH ₂ (1.1 eq), (Ph ₃ P) ₃ RhCl, 0° to rt, 2 h PhSiH ₃ (1.01 eq), Ni, PPh ₃ (0.02 eq)	 (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)  (100)	83 435 435 438 79, 83
	(EtO) ₃ SiH (1.1 eq), CsF (1 eq), rt, 1 h Me(EtO) ₂ SiH (1.1 eq), CsF (1 eq), rt, 2 h Ph ₂ SiH ₂ (0.5 eq), salt	 (80)  (95)  (95)	79 79, 83 319
	Salt HCO ₂ K KF C ₆ H ₄ (CO ₂ K) ₂ -1,2 CsF	(85) (65) (65) (100)	




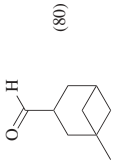
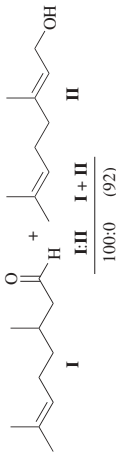
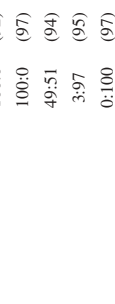

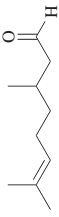







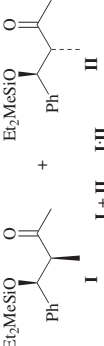
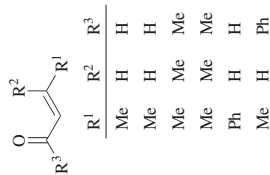
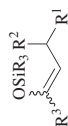
PMHS (1 eq), ZnCl ₂ (1 eq), Et ₂ O, rt, 24 h	I (69)	315
Me(EtO) ₂ SiH (2.3 eq), CsF (1 eq), rt, 2 h	I (95)	83
(EtO) ₂ SiH (2.3 eq), KF (1 eq), rt, 24 h	I (95)	83
(EtO) ₂ SiH, CsF, rt, 5 min	I (100)	83
Et ₃ SiH (1.5 eq), CsF (1.5 eq), MeCN, rt, 10 h		76
PhMe ₂ SiH (1.2 eq), TBAF (2 eq), HMPA, rt, 0.5 h		320
Et ₃ SiH (0.72 eq), H ₂ PtCl ₆		76
PhSiH ₃ (1.5 eq), [(Ph ₃ P)(CuH)] ₆ (5 mol%), MeC ₆ H ₅ , 5 h		447
R ₃ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl		435
R ₃ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl		435
Et ₃ SiD (1.1 eq), (Ph ₃ P) ₃ RhCl		435
Ph ₂ SiH ₂ (2.0 eq), ZnCl ₂ (0.12 eq), (Ph ₃ P) ₄ Pd (0.012 eq), CHCl ₃ , rt, 1.5 h		436

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES

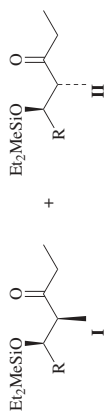
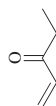
Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	Et_3SiH (3 eq), TFA (10 eq), CCl_4 , 50° , 6 h	 (94)	434, 439
	PMHS, Pd/C, EtOH, 80°	 (100)	316
	PMHS-Pd nanocomposite, C_6H_6 , rt, 5 h	 I (95)	219
	$PhMe_2SiH$ (1.1 eq), $(Ph_3P)_4RhH$ (0.5 mol%), CH_2Cl_2 , 50° , 24 h	 (73), E:Z = 33:67	374
	$ClCH_2Me_2SiH$ (1.1 eq), $(Ph_3P)_4RhH$ (0.2 mol%), CH_2Cl_2 , rt, 1.56 h	 (85), E:Z = 1:2	374
	$(EtO)_3SiH$ (1.1 eq), $(Ph_3P)_4RhH$ (0.3 mol%), CH_2Cl_2 , rt, 20 h	 (75), E:Z = 56:44	374
	$Ph-C(=O)-H$, Et_2MeSiH , $Rh_4(CO)_{12}$ (0.5 mol %), solvent		464
	Solvent	<div> <div>I + II</div> <div>(42)</div> </div>	50:50
	Temp	<div> <div>I + II</div> <div>(97)</div> </div>	77:23
	Time	<div> <div>I + II</div> <div>(95)</div> </div>	86:14
		<div> <div>I + II</div> <div>(85)</div> </div>	88:12
		<div> <div>I + II</div> <div>(64)</div> </div>	81:19
		<div> <div>I + II</div> <div>(98)</div> </div>	87:13
		<div> <div>I + II</div> <div>(93)</div> </div>	85:15
		<div> <div>I + II</div> <div>(53)</div> </div>	78:22

C₄₋₁₀R₃SiH (1 eq), (Ph₃P)₃RhCl (0.5 mol%)

R ₃ Si	Temp	Time
Et ₃ Si	60°	15 min
Ph ₃ Si	60°	30 min
Et ₃ Si	50°	15 min
PhMe ₂ Si	50°	30 min
Et ₃ Si	60°	15 min
Et ₃ Si	60°	30 min

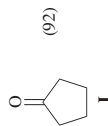


411

C₅Et₂MeSiH, Rh₄(CO)₁₂ (0.5 mol%),
ligand, RCHO, hexane

R	Ligand	Temp	Time
<i>n</i> -C ₅ H ₉	none	0°	6.5 h
<i>n</i> -C ₅ H ₉	MePh ₃ P	15°	6 h
Ph	MePh ₃ P	0°	20 h

464

Cl₃SiH (2 eq), CoCl₂ (0.175 eq), neat;
or CD₃CN, DMI (0.5 eq), rt, 5 h

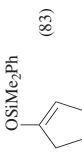
451

PhMe₂SiH (2 eq), CoCl₂ (0.175 eq),
DMI (0.5 eq), 80°, 10 h

I (65)

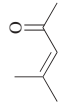
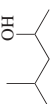
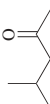
Ph₂SiH₂ (1.2 eq), ZnCl₂ (0.16 eq),
(Ph₃P)₄Pd (0.005 eq), CHCl₃, rt, 0.5 h

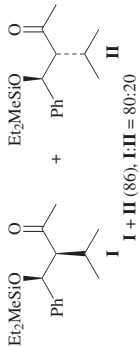
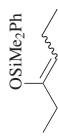
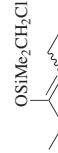
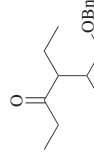
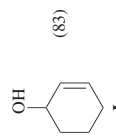
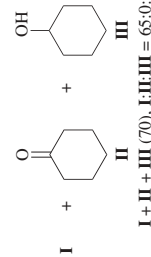
I (99)

PhMe₂SiH (1.1 eq),
(Ph₃P)₄RhH (0.3 mol%),
CH₂Cl₂, rt, 12 h

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TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₆	Et ₃ SiH (3 eq), TFA (6 eq), CHCl ₃ , 60°, 4 h	 I (90)	434
	Et ₃ SiH (1.2 eq), TiCl ₄ (2.4 eq), CH ₂ Cl ₂ , -5°, 1 h	 II (75)	449
	Ph ₂ SiH ₂ (2.0 eq), ZnCl ₂ (0.35 eq), (Ph ₃ P) ₃ Pd (0.007 eq), CHCl ₃ , rt, 1 h	II (99)	436
	Et ₃ SiH (3 eq), AlCl ₃ (1.2 eq), HCl, CH ₂ Cl ₂ , rt, 4 h	I (71) + II (10)	136
	R ₃ SiH (1.1 eq), (Ph) ₃ P ₃ RhCl	I + II	435
	R ₃ Si	I + II	
	EtMe ₂ Si	(99) 0:100	
	PhMe ₂ Si	(98) 1:99	
	Et ₃ Si	(95) 1:99	
	(<i>i</i> -Pr) ₂ HSi	(93) 13:87	
	Et ₃ HSi	(90) 57:43	
	PhMeHSi	(98) 61:39	
	Ph ₂ HSi	(99) 93:7	
	PhH ₂ Si	(95) 99:1	
	Ph ₂ SiH ₂ (1.3-1.5 eq), Mo(CO) ₆ (3-5 mol%), THF, reflux, 24 h	II (5)	450
	PhSiH ₃ (1.3-1.5 eq), Mo(CO) ₆ (3-5 mol%), THF, reflux, 23 h	II (95)	450

<p>PhCHO, Et₂MeSiH, Rh₄(CO)₁₂ (0.5 mol%), MePh₂P, C₆H₆, 20°, 7 h</p>	 <p>I + II (86), I:II = 80:20</p>	464
<p>PhCHO, Et₂MeSiH, Rh₄(CO)₁₂ (0.5 mol%), C₆H₆, 20°, 7 h</p>	<p>I + II (0)</p>	464
<p>PhMe₂SiH (1.1 eq), (Ph₃P)₄RhH (0.2 mol%), CH₂Cl₂, rt, 6 h</p>	 <p>(82), E:Z = 77:23</p>	374
<p>Cl[CH₂Me₂SiH (1.1 eq), (Ph₃P)₄RhH (0.3 mol%), CH₂Cl₂, rt, 10 h</p>	 <p>(83), E:Z = 4:1</p>	374
<p>1. HMMe₂SiOSiMe₂H (1.5 eq), 1/6 [(Ph₃P)(CuH)]₆ (5 mol%), MeC₆H₅, rt, 1 h 2. BrOCH₂CHO, TiCl₄, CH₂Cl₂, -78°</p>	 <p>(79)</p>	455
<p>Ph₂SiH₂ (1.3 eq), (Ph₃P)₄RhH (0.4 mol%), CH₂Cl₂, rt, 4 h</p>	 <p>(83)</p>	374
<p>Ph₂SiH₂ (0.5 eq), <i>o</i>-C₆H₄(CO₂K)₂, 140°, 1.5 h</p>	 <p>I + II + III (70), I:II:III = 65:0:35</p>	319

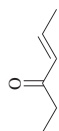
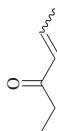

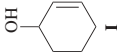




TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₆	Ph ₂ SiH ₂ (0.5 eq), CsF, 140°, 1.5 h	 I +  II +  III I + II + III (65), I:II:III = 60:10:30	319
	G , 0°, 2 h	I (85)	93
	H , 0°, 5 h	I + II (91), I:II = 97:3	93
	PhMe ₂ SiH (4 eq), CuCl (2 eq), DMI, rt, 22 h	III (100)	445
	PhMe ₂ SiH (2 eq), DMA, (Ph ₃ P) ₃ CuF•2 EtOH (1 eq)	III (91)	446
	1. PhMe ₂ SiH (2 eq), (Ph ₃ P) ₃ CuF•2 EtOH, DMA, 0°, 0.5 h 2. Add enone, 0° to rt, 2 h	III (92)	444
	PhMe ₂ SiH (1.2 eq), CuCl (50 mol%), PPh ₃ (50 mol%), TBAF (25 mol%), DMA, 0° to rt, 17 h	III (67)	444
	PhMe ₂ SiH (2 eq), (Ph ₃ P) ₃ CuF•2 EtOH (1.0 eq), DMA, 0° to rt, 2 h	II (92)	444
	PhMe ₂ SiH (1.2 eq), CuCl (50 mol%), PPh ₃ (50 mol%), TBAF (20 mol%), DMA, 0° to rt, 17 h	II (67) ^a	444
	Ph ₂ SiH ₂ (1.2 eq), ZnCl ₂ (0.16 eq), (Ph ₃ P) ₄ Pd (0.005 eq), rt, 0.5 h	II (100)	436

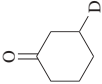
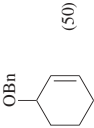

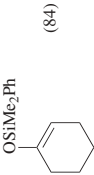
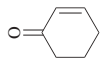
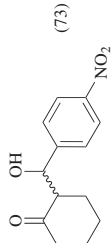
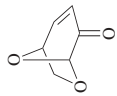
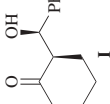
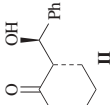
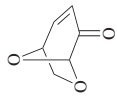
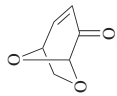
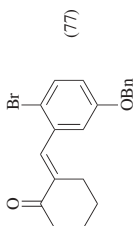
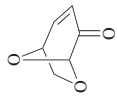
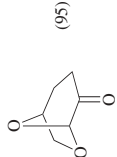
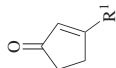
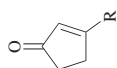
PhSiH ₃ (1.5 eq), [(Ph ₃ P)CuH] ₆ (5 mol%), MeC ₆ H ₅ , 8 min	II (100)	447
PhSiH ₃ (1.01 eq), Ni, PPh ₃ (0.02 eq)	II (93.1)	438
PhSiH ₃ (1.3-1.5 eq), Mo(CO) ₆ (3-5 mol%), THF, reflux, 4 h	II (25)	450
Cl ₃ SiH (2 eq), CoCl ₂ (0.175 eq), CD ₃ CN, DMI (0.5 eq), rt, 5 h	II (88)	451
Cl ₃ SiH (2 eq), CoCl ₂ (0.05 eq), neat, or CD ₃ CN, DMPU (0.25 eq), rt, 5 h	II (88)	451
L-D , CH ₂ Cl ₂ , rt, 2 h		101
Et ₃ SiH (1 eq), TMSOTf (0.1 eq), BnOTMS (0.83 eq), CH ₂ Cl ₂ , -78° to -30°	 (50)	341
ClCH ₂ Me ₂ SiH (1.1 eq), (Ph ₃ P) ₄ RhH (0.1 mol%), CH ₂ Cl ₂ , rt, 0.5 h	 (83)	374
PhMe ₂ SiH (1.1 eq), (Ph ₃ P) ₄ RhH (0.3 mol%), CH ₂ Cl ₂ , rt, 12 h	 (84)	374

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. PhMe_2SiH , (1.5 eq), 1/6 $[\text{CuH}(\text{PPh}_3)]_6$ (5 mol %), MeC_6H_5 , rt, 1 h 2. $4\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$, $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , -78°	 (73)	455
	Et_2MeSiH , PhCHO , $\text{Rh}_4(\text{CO})_{12}$ (0.5 mol %), MeC_6H_5 , 15° , 15 h	 I +  II I + II (57), I:II = 75:25	464
	Et_2MeSiH , PhCHO , $\text{Rh}_4(\text{CO})_{12}$ (0.5 mol %), I + II (75), I:II = 73:27 MePh_2P , MeC_6H_5 , 0° , 5 h		464
	1. PhMe_2SiH (1.5 eq), 1/6 $[\text{CuH}(\text{PPh}_3)]_6$ (5 mol %), MeC_6H_5 , rt 2. 2-Br-5-benzoyloxybenzaldehyde, $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 3. TsOH (cat.), C_6H_6 , reflux, 1.5 h	 (77)	455
	Ph_2SiH_2 (2.0 eq), ZnCl_2 (1.0 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (0.10 eq), CHCl_3 , rt, 1 h	 (95)	436

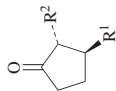


R ¹
Me
Me
Me
BnCH ₂
BnCH ₂
BnCH ₂
BnCH ₂

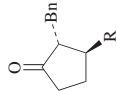


R
Me
Me
Me
BnCH ₂
BnCH ₂
BnCH ₂
BnCH ₂

1. Ph₂SiH₂ (0.53 eq), CuCl (5%), NaOBu-*t* (5%), (*S*)-*p*-Tol-BINAP, MeC₆H₅, 0°, 2-3 h
2. R²X, TBAT (1.2 eq), CH₂Cl₂/MeC₆H₅ (1:1), rt, 24 h



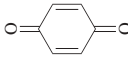
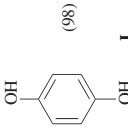
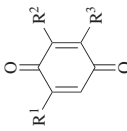
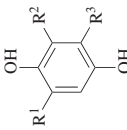
R ² X	dr
BnBr	(62) 92:8
BrCH ₂ CO ₂ Et	(52) 94:6
1-Bromo-3-methyl-2-butene	(52) 80:20
BnBr	(67) 94:6
Allyl bromide	(64) 76:24
MeI	(65) 73:27
<i>n</i> -BuI	(42) 85:15

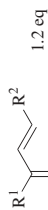


1. Ph₂SiH₂ (0.53 eq), CuCl (5%), NaOBu-*t* (5%), (*S*)-*p*-Tol-BINAP, MeC₆H₅, 0°, 2-3 h
2. BnBr, TBAT (1.2 eq), solvent

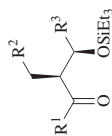
Solvent	Temp
CH ₂ Cl ₂	rt
THF	rt
CH ₂ Cl ₂ :MeC ₆ H ₅ (1:1)	rt
CH ₂ Cl ₂	50
CH ₂ Cl ₂ :MeC ₆ H ₅ (1:1)	rt
CH ₂ Cl ₂ :MeC ₆ H ₅ (1:1)	rt
CH ₂ Cl ₂ :MeC ₆ H ₅ (1:1)	rt

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₆</div> 	Et ₃ SiH (1.5 eq), TFA, (13 eq), 60-65°, 1 h	 (98)	393
	PMHS (10% xs), (Bu ₃ AcO)Sn ₂ O (2 mol%), EtOH, reflux	I (81)	316
<div>C₆₋₉</div> 	HMe ₂ SiOSiMe ₂ H (1.5 eq), NaI (10 mol%), TMSCl (10 mol%), CH ₂ Cl ₂ , reflux, 30 min	 (85) (96) (90) (98) (90)	314, 357





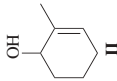
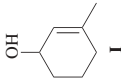


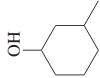

Et₃SiH (1 eq), InBr₃ (10 mol%),
R³CHO (1 eq), EtCN, -78° to rt, 1h



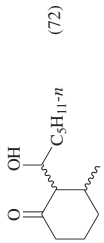
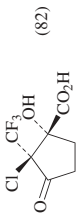
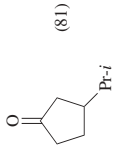
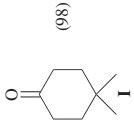


760

R ¹	R ²	R ³	syn:anti
Et	Me	4-MeOC ₆ H ₄	(61) >99:1
Et	Me	Ph	(40) >99:1
Me	Ph	4-MeOC ₆ H ₄	(46) >99:1
Ph	Me	4-MeOC ₆ H ₄	(75) 90:10
Ph	Me	4-O ₂ NC ₆ H ₄	(59) >99:1
Ph	Me	Ph	(78) 92:8
Ph	Me	Bn	(40) >99:1
Ph	Me	<i>t</i> -Bu	(73) >99:1
Ph	Me	Et ₂ CH	(87) 90:10
Ph	Ph	4-MeOC ₆ H ₄	(82) >99:1
Ph	Ph	Ph	(65) 78:22

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₇	Et ₃ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), 45°, 4 h	 +  I (90), I:II = 98:2	435
	TMSH (1.2 eq), TiCl ₄ (2.4 eq), CH ₂ Cl ₂ , -5°, 1 h	I (73)	449
	Et ₃ SiH (1.2 eq), TiCl ₄ (2.4 eq), CH ₂ Cl ₂ , -5°, 1 h	I (73)	449
	Ph ₂ SiH ₂ (1.3 eq), (Ph ₃ P) ₄ RhH (0.3 mol%), CH ₂ Cl ₂ , rt, 4 h	 I	374
	Et ₃ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), 50°, 30 h	 I +  II (97), I:II = 0:100	435
	Ph ₂ SiH ₂ (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), 0°, 340 min	II (97), II:I = 100:0	435
	PhSiH ₃ (1.5 eq), [(Ph ₃ P)CuH] ₆ (5 mol%), MeC ₆ H ₅ , 18 h	II (100)	447
	PhSiH ₃ (1.01 eq), Ni, PPh ₃ (0.02 eq)	II (100)	438
	Et ₃ SiH (1.2 eq), TiCl ₄ (2.4 eq), CH ₂ Cl ₂ , -5°, 1 h	II (74)	449

<p>HMMe₂SiOSiMe₂H (1.5 eq), 1/6 [(Ph₃P)CuH]₆ (5 mol%), MeC₆H₅, rt, 24 h</p>	 (85)	455
<p>PhMe₂SiH (1.1 eq), (Ph₃P)₄RhH (0.5 mol%), CH₂Cl₂, 50°, 24 h</p>	 (89)	374
<p>1. HMMe₂SiOSiMe₂H (1.5 eq), 1/6 [(Ph₃P)CuH]₆ (5 mol%), MeC₆H₅, rt, 39 h 2. <i>n</i>-C₅H₁₁CHO, TiCl₄, CH₂Cl₂, -78°</p>	 (72)	455
<p>Et₃SiH (3 eq), TFA, rt, 48 h</p>	 (82)	453
<p>PMHS (1.6 eq), 209 (0.1 mol%), NaOBu-<i>t</i> (0.1 mol%), MeC₆H₅, rt, 1 h</p>	 (81)	454
<p>PhSiH₃ (1.01 eq), Ni, PPh₃ (0.02 eq)</p>	 (98)	438
<p>PhSiH₃ (1.5 eq), [(Ph₃P)CuH]₆ (5 mol%), MeC₆H₅, 8 min</p>	<p>I (85)</p>	447

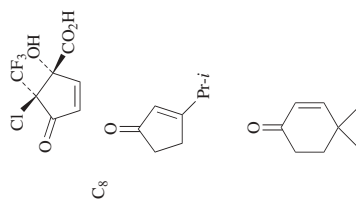
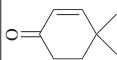
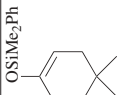
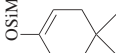
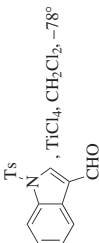
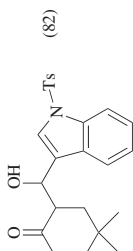
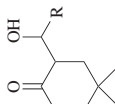
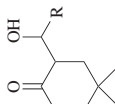
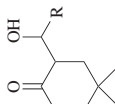
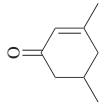
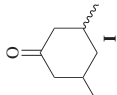


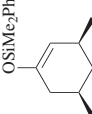
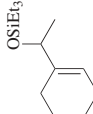
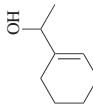
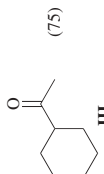
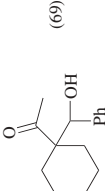


TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.						
 C ₈	PhMe ₂ SiH (1.1 eq), (Ph ₃ P) ₄ RhH (0.4 mol%), CH ₂ Cl ₂ , rt, 12 h	 (96)	374						
	ClCH ₂ Me ₂ SiH (1.1 eq), (Ph ₃ P) ₄ RhH (0.3 mol%), CH ₂ Cl ₂ , rt, 4 h	 (80)	374						
	1. PhMe ₂ SiH (1.5 eq), 1/6 [(Ph ₃ P)CuH] ₆ (5 mol%), MeC ₆ H ₅ , rt, 4 h 2.  , TiCl ₄ , CH ₂ Cl ₂ , -78°	 (82)	455						
	1. PhMe ₂ SiH, (1.5 eq), [(Ph ₃ P)CuH] ₆ (18 mol%), MeC ₆ H ₅ , rt, 4 h 2. Aldehyde, BF ₃ •OEt ₂ , CH ₂ Cl ₂ , -78°, 1 h	<table><tr><th>Aldehyde</th><th>R</th></tr><tr><td></td><td>cyclohex-3-en-1-carbaldehyde (80)</td></tr><tr><td></td><td>4-O₂NC₆H₄CHO (68)</td></tr></table>	Aldehyde	R		cyclohex-3-en-1-carbaldehyde (80)		4-O ₂ NC ₆ H ₄ CHO (68)	455
Aldehyde	R								
	cyclohex-3-en-1-carbaldehyde (80)								
	4-O ₂ NC ₆ H ₄ CHO (68)								
	PhMe ₂ SiH (4 eq), CuCl (2 eq), DMI, rt, 22 h	 (100) cis:trans = 97:3	445						
	Cl ₃ SiH (2 eq), CoCl ₂ (0.175 eq), CD ₃ CN, DMI (0.5 eq), rt, 12 h PhSiH ₃ (1.5 eq), [(Ph ₃ P)CuH] ₆ (5 mol %), MeC ₆ H ₅ , 46 h	 I (50)	451						
		 I (100), single isomer	447						

 (87) cis:trans = 92:8	<p>PhMe₂SiH (1.1 eq), (Ph₃P)₄RhH (0.5 mol%), CH₂Cl₂, 50°, 24 h</p>	374
<p>Et₃SiH (1.1 eq), (Ph₃P)₃RhCl (10 mol%), C₆H₆, 50°, 5 h</p>	<p>  +  I II I (95), I:II = 87:13 </p>	435
<p>Cl₃SiH (2 eq), CoCl₂ (0.175 eq), CD₃CN, DMI (0.5 eq), rt, 2 h</p>	<p>  III III (100) </p>	451
<p>PhSiH₃ (1.3-1.5 eq), Mo(CO)₆ (3-5 mol%), THF, reflux, 4.5 h</p>	<p> III (—) </p>	450
<p>Ph₂SiH₂ (1.8 eq), ZnCl₂ (0.38 eq), (Ph₃P)₄Pd (0.013 eq), rt, 4 h</p>	<p> III (85) </p>	436
<p>Ph₂SiH₂ (1.8 eq), ZnCl₂ (0.38 eq), (Ph₃P)₄Pd (0.013 eq), CHCl₃, rt, 4 h</p>	<p> III (97) </p>	219
<p>PMHS-Pd nanocomposite, C₆H₆, rt, 6 h</p>	<p> I + II (96), I:II = 97:3 </p>	435
<p>Ph₂SiH₂ (1.1 eq), (Ph₃P)₃RhCl (10 mol%), C₆H₆, rt, 1 h</p>	<p>  (69) </p>	464

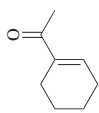
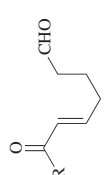
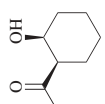
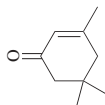
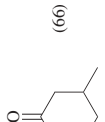
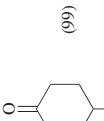
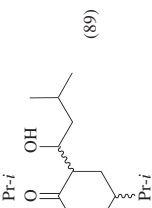
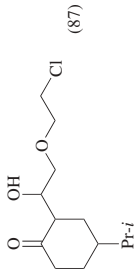
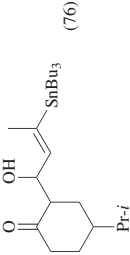
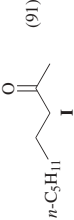


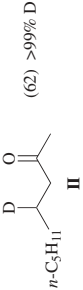



TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C_{8,17}</p>  <p>R</p> <p>Me</p> <p>Ph</p> <p>4-CF₃C₆H₅</p> <p>2-C₁₀H₇</p> <p>2-C₄H₃O</p> <p>2-C₄H₃S</p>	<p>PhSiH₃ (1.2 eq), Co(dpm)₂ (5 mol%), rt</p>	 <p>(38)</p> <p>(87)</p> <p>(72)</p> <p>(68)</p> <p>(75)</p> <p>(73)</p>	461
<p>C₉</p> 	<p>TMOSH (1.2 eq), TiCl₄ (2.4 eq), CH₂Cl₂, -5°, 1 h</p> <p>Et₃SiH (1.2 eq), TiCl₄ (2.4 eq), CH₂Cl₂, -5°, 1 h</p> <p>PhMe₂SiH (4 eq), CuCl (2 eq), DML, rt, 20 h</p> <p>PhSiH₃ (1.5 eq), [(Ph₃P)CuH]₆ (0.5 mol%), MeC₆H₅, 6 h</p> <p>1. PhMe₂SiH (2.5 eq), 1/6 [(Ph₃P)CuH]₆ (5 mol%), MeC₆H₅, rt, 3 h 2. Me₂CHCH₂CHO, BF₃•OEt₂, CH₂Cl₂, -78°</p>	 <p>(66)</p> <p>I (53)</p> <p>I (13)</p>  <p>(99)</p>  <p>(89)</p>	449 449 445 447 455

1. PhMe_2SiH (1.5 eq), 1/6 $[(\text{Ph}_3\text{P})\text{CuH}]_6$ (5 mol%), MeC_6H_5 , rt, 2 h 2. $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CHO}$, $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , -78°		455
1. PhMe_2SiH (1.5 eq), 1/6 $[(\text{Ph}_3\text{P})\text{CuH}]_6$ (5 mol%), MeC_6H_5 , rt, 2 h 2. $\text{Bu}_3\text{Sn}-\text{CH}=\text{CH}-\text{CHO}$, $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , -78°		455
PhMe_2SiH (2 eq), DMA, $(\text{Ph}_3\text{P})_3\text{CuF}\cdot 2\text{EtOH}$ (1 eq)		446
1. PhMe_2SiH (2 eq), $(\text{Ph}_3\text{P})_3\text{CuF}\cdot 2\text{EtOH}$, DMA, 0° , 0.5 h 2. Add enone, 0° to rt, 2.5 h		444
PhMe_2SiH (1.2 eq), CuCl (25 mol%), PPh_3 (25 mol%), TBAF (20 mol%), DMA, 0° to rt, 2 h		444
1. PhMe_2SiD (2 eq), $(\text{Ph}_3\text{P})_3\text{CuF}\cdot 2\text{EtOH}$, DMA, 0° , 0.5 h 2. Add enone, 0° to rt, 2.5 h		444
PhMe_2SiH , CuCl (25 mol%), PPh_3 (25 mol%), TBAF (20 mol%), DMA, 0° to rt, 2 h		444

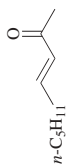
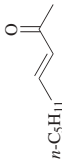
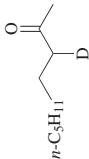
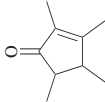
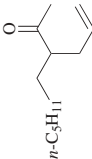
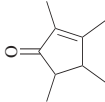
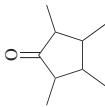


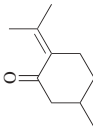
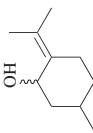
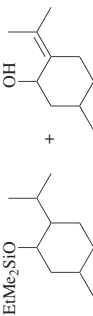
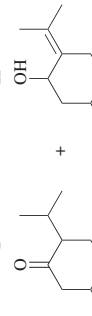


TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₉</p> 	<p>1. PhMe₂SiH (2 eq), (Ph₃P)₅CuF•2 EtOH, DMA, 0°, 0.5 h 2. Add enone, 0°, 45 min 3. D₂O</p>	 <p>(67) 85% D</p>	444
	<p>1. PhMe₂SiH (2 eq), (Ph₃P)₅CuF•2 EtOH, DMA, 0°, 0.5 h 2. Add enone, 0°, 45 min 3. Allyl bromide</p>	 <p>(45)</p>	444
	PhSiH ₃ (1.01 eq), Ni, PPh ₃ (0.02 eq)	 <p>(81.9)</p>	438
<p>C₁₀</p> 	PhSiH ₃ (1.3 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE	 <p>(74)</p>	448
	Et ₂ SiH ₂ , (Ph ₃ P) ₃ RhCl	 <p>(—)</p>	435
	EtMe ₂ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), C ₆ H ₆ , rt, 2 h	 <p>I (97), I:II = 78:22</p>	435
	Ph ₂ SiH ₂ (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), rt, 20 min	 <p>I (98), I:II = 0:100</p>	435

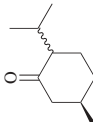
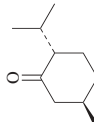
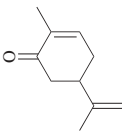
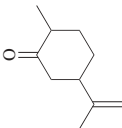
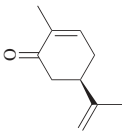
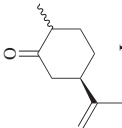
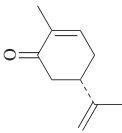

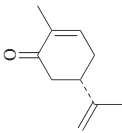
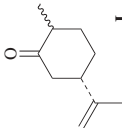
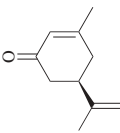

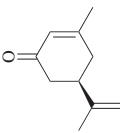

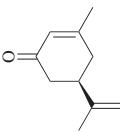

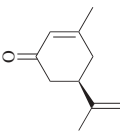
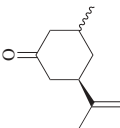
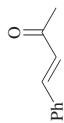
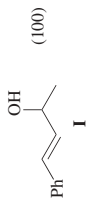
<p> Ph_2SiH_2 (1.55 eq), ZnCl_2 (0.4 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (0.018 eq), CHCl_3, rt, 3 h </p>		(9S) cis:trans = 1:1	436																			
<p> R_3SiH, $(\text{Ph}_3\text{P})_3\text{RhCl}$ </p> <table border="1"> <thead> <tr> <th>R_3Si</th> <th>$\text{I} + \text{II}$ (—)</th> <th>$\text{I}:\text{II}$</th> </tr> </thead> <tbody> <tr> <td>PhMe_2Si</td> <td>75:25</td> <td></td> </tr> <tr> <td>Et_3Si</td> <td>50:50</td> <td></td> </tr> <tr> <td>$(n\text{-Pr})_3\text{Si}$</td> <td>50:50</td> <td></td> </tr> <tr> <td>Et_2HSi</td> <td>0:100</td> <td></td> </tr> <tr> <td>Ph_2HSi</td> <td>0:100</td> <td></td> </tr> </tbody> </table>	R_3Si	$\text{I} + \text{II}$ (—)	$\text{I}:\text{II}$	PhMe_2Si	75:25		Et_3Si	50:50		$(n\text{-Pr})_3\text{Si}$	50:50		Et_2HSi	0:100		Ph_2HSi	0:100				437	
R_3Si	$\text{I} + \text{II}$ (—)	$\text{I}:\text{II}$																				
PhMe_2Si	75:25																					
Et_3Si	50:50																					
$(n\text{-Pr})_3\text{Si}$	50:50																					
Et_2HSi	0:100																					
Ph_2HSi	0:100																					
<p> R_3SiH (1.1 eq), $(\text{Ph}_3\text{P})_3\text{RhCl}$ (0.5 mol%), 50°, 2 h </p> <table border="1"> <thead> <tr> <th>R_3Si</th> <th>$\text{I} + \text{II}$ (—)</th> <th>$\text{I}:\text{II}$</th> </tr> </thead> <tbody> <tr> <td>Et_3Si</td> <td>50:50</td> <td></td> </tr> <tr> <td>$(n\text{-Pr})_3\text{Si}$</td> <td>50:50</td> <td></td> </tr> <tr> <td>PhMe_2Si</td> <td>75:25</td> <td></td> </tr> <tr> <td>Et_2HSi</td> <td>0:100</td> <td></td> </tr> <tr> <td>Ph_2HSi</td> <td>0:100</td> <td></td> </tr> </tbody> </table>	R_3Si	$\text{I} + \text{II}$ (—)	$\text{I}:\text{II}$	Et_3Si	50:50		$(n\text{-Pr})_3\text{Si}$	50:50		PhMe_2Si	75:25		Et_2HSi	0:100		Ph_2HSi	0:100					438
R_3Si	$\text{I} + \text{II}$ (—)	$\text{I}:\text{II}$																				
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Ph_2HSi	0:100																					
<p> Et_2SiH_2, $(\text{Ph}_3\text{P})_3\text{RhCl}$ </p> <table border="1"> <thead> <tr> <th>R_3Si</th> <th>$\text{I} + \text{II}$ (—)</th> <th>$\text{I}:\text{II}$</th> </tr> </thead> <tbody> <tr> <td>Et_3Si</td> <td>50:50</td> <td></td> </tr> <tr> <td>$(n\text{-Pr})_3\text{Si}$</td> <td>50:50</td> <td></td> </tr> <tr> <td>PhMe_2Si</td> <td>75:25</td> <td></td> </tr> <tr> <td>Et_2HSi</td> <td>0:100</td> <td></td> </tr> <tr> <td>Ph_2HSi</td> <td>0:100</td> <td></td> </tr> </tbody> </table>	R_3Si	$\text{I} + \text{II}$ (—)	$\text{I}:\text{II}$	Et_3Si	50:50		$(n\text{-Pr})_3\text{Si}$	50:50		PhMe_2Si	75:25		Et_2HSi	0:100		Ph_2HSi	0:100			<p> $\text{I} + \text{II}$ (100) $\text{I}:\text{II} = 4.5:1$ </p>	439	
R_3Si	$\text{I} + \text{II}$ (—)	$\text{I}:\text{II}$																				
Et_3Si	50:50																					
$(n\text{-Pr})_3\text{Si}$	50:50																					
PhMe_2Si	75:25																					
Et_2HSi	0:100																					
Ph_2HSi	0:100																					
<p> Ph_2SiH_2 (1.3–1.5 eq), $\text{Mo}(\text{CO})_6$ (3–5 mol%), THF, reflux, 15 h </p>		<p> $\text{I} + \text{II}$ (90), $\text{I}:\text{II} = 4.5:1$ </p>	440																			
<p> PhSiH_3 (1.3–1.5 eq), $\text{Mo}(\text{CO})_6$ (3–5 mol%), THF, reflux, 3 h </p>		<p> $\text{I} + \text{II}$ (90), $\text{I}:\text{II} = 4.5:1$ </p>	441																			

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMe_2SiH (4 eq), DMA, (Ph_3P) $_3\text{CuF}\cdot 2$ EtOH (1 eq)	 (85) dr = 8:1	446
	1. PhMe_2SiH (2 eq), (Ph_3P) $_3\text{CuF}\cdot 2$ EtOH, DMA, 0° , 0.5 h 2. Add enone, 0° to rt, 24 h	 (85)	444
	PhMe_2SiH , CuCl (160 mol%), PPh_3 (160 mol%), TBAF (150 mol%), DMA, 0° to rt, 4.5 h	 I (87)	444
	PhMe_2SiH (4 eq), CuCl (2 eq), DMI, rt, 22 h	 (83)	445
	Ph_2SiH_2 (1.7 eq), ZnCl_2 (0.52 eq), (Ph_3P) $_2\text{Pd}$ (0.013 eq), CHCl_3 , rt, 2 h	 I (89) cis:trans = 1:4	436
	PhSiH_3 (2 eq), $\text{Mn}(\text{dpm})_3$ (3 mol%), <i>i</i> -PrOH	 I (50)	448
	PhSiH_3 (1.3–1.5 eq), $\text{Mo}(\text{CO})_6$ (3–5 mol%), THF, reflux, 11.5 h	 I (0)	450
	Ph_2SiH_2 (1.3 eq), (Ph_3P) $_4\text{RhH}$ (0.4 mol%), CH_2Cl_2 , rt, 12 h	 (84) cis:trans = 65:35	374



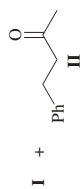
(EtO)₃SiH, CsF, rt, 30 min



83

Ph₂SiH₂ (0.5 eq), CsF, rt, 30 min

R₃SiH (x eq), DMA,
(Ph₃P)₃CuF•2 EtOH (y eq)



319

446

R ₃ Si	x	y
PhMe ₂ Si	2	1
PhMe ₂ Si	1	1
PhMe ₂ Si	2	0.05
Et ₃ Si	2	1
Ph ₂ HSi	2	1
PhCl ₂ Si	2	1

I	II
(—)	(>99)
(—)	(63)
(trace)	(69)
(—)	(95)
(36)	(49)
(—)	(—)

R₃SiH (2 eq),
(Ph₃P)₃CuF•2 EtOH (1.0 eq),
DMA, 0° to rt, 0.5 h

444

I + **II**

R ₃ Si	Time
PhMe ₂ Si	2 h
Et ₃ Si	1.5 h
(EtO) ₃ Si	3.5 h
Ph ₂ HSi	18 h
PhCl ₂ Si	—

I	II
(—)	(>99)
(—)	(96)
(34)	(58)
(36)	(49)
(0)	(0)

Et₃SiH (1.1 eq), (Ph₃P)₃RhCl,
45°, 15 h

I:II = 37:63

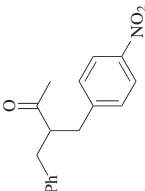
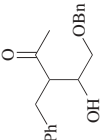
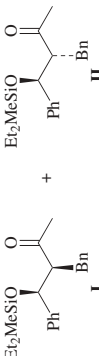
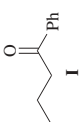
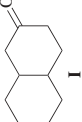
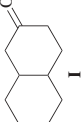
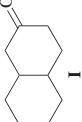
435

Ph₂SiH₂ (1.1 eq), (Ph₃P)₃RhCl,
0° to rt, 6 h

I:II = 60:40

435

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

PhSiH ₃ (1.3-1.5 eq), Mo(CO) ₆ (3-5 mol%), THF, reflux, 1.5 h	II (100)	450
PhSiH ₃ (1.01 eq), Ni, PPh ₃ (0.02 eq)	II (96.9)	438
1. HMe ₂ SiOSiMe ₂ H (0.55 eq), 1/6 [(Ph ₃ P)CuH] ₆ (2 mol%), MeC ₆ H ₅ , rt, 2 h 2. 4-O ₂ NC ₆ H ₄ CH ₂ Br, CH ₂ Cl ₂ , rt, 3 h	 (57)	455
1. PMHS (1.25 eq), 1/6 [(PPh ₃)CuH] ₆ (2 mol%), MeC ₆ H ₅ , rt 2. BnOCH ₂ CHO, TiCl ₄ , CH ₂ Cl ₂ , -78°	 (83)	455
PhCHO, Et ₃ MeSiH, Rh ₄ (CO) ₁₂ (0.5 mol%), MePh ₂ P, C ₆ H ₆ , 20°, 3.5 h	 I + II (88), I:II = 80:20	464
Et ₃ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl, 45°, 15 h	 I (—)	435
Ph ₂ SiH ₂ (1.1 eq), (Ph ₃ P) ₃ RhCl, 0° to rt, 6 h	 I (—)	435
Et ₃ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), 80°, 25 h	 I (96), I:II = 94:6	435
Et ₃ SiH ₂ (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), 0°, 30 min	 I (98), I:II = 3:97	435

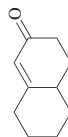
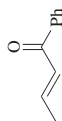
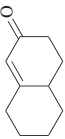
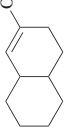
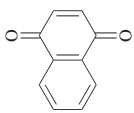
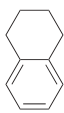
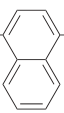
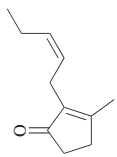
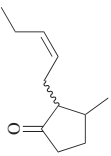
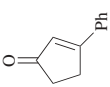
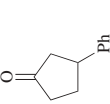
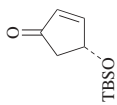
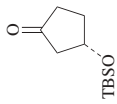
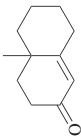
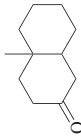


TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (1 eq), $(\text{Ph}_3\text{P})_3\text{RhCl}$ (0.5 mol%), 50° , 60 min	 OSiEt ₃ (92)	411
	Et_3SiH (4 eq), TFA (20 eq), 60–65°, 8 h	 (50)	393
	Et_3SiH (5 eq), TFA (26 eq), 60–65°, 10 h	 I (75)	393
	$\text{HMe}_2\text{SiOSiMe}_2\text{H}$ (1.5 eq), NaI (10 mol%), TMSCl (10 mol%), CH_2Cl_2 , reflux, 30 min	I (75)	314
 C ₁₁	PMHS (1.6 eq), 209 , NaOBu- <i>t</i> (0.1 mol%), MeC_6H_5 , rt, 1 h	 (85) dr = 4:1	454
	PMHS (1.6 eq), 209 (0.1 mol%), NaOBu- <i>t</i> (0.1 mol%), MeC_6H_5 , rt, 1 h	 (95)	454
	PhSiH_3 (1.5 eq), $[(\text{Ph}_3\text{P})\text{CuH}]_6$ (5 mol%), MeC_6H_5 , 10 min	 (70)	447
	Et_3SiH (1.2 eq), TiCl_4 (2.4 eq), CH_2Cl_2 , 1 h	 TBSO	449

Temp
 0° (53) cis:trans = 9:1
 -78° (50)

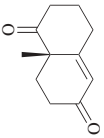
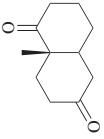
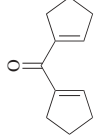
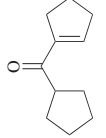
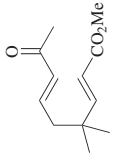
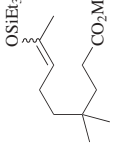
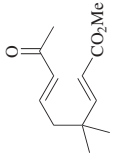
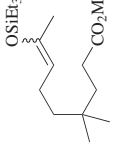
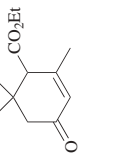
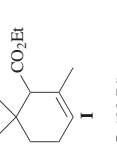
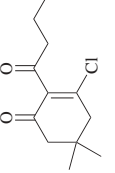
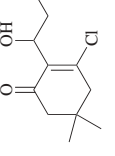
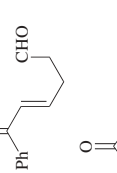
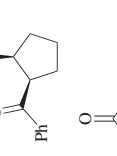
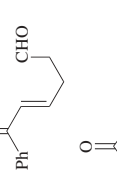
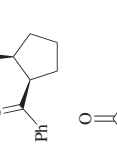
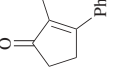
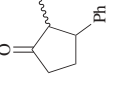
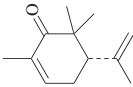
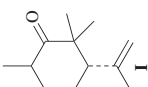
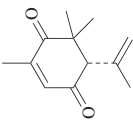
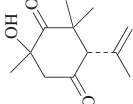
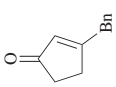
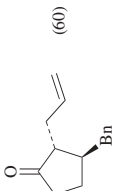
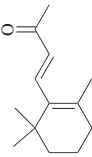
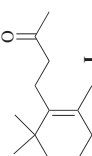
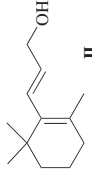
		PhMe ₂ SiH (4 eq), CuCl (2 eq), DMI, rt, 21 h	(81) cis:trans = 98:2	445
		Et ₃ SiH (2 eq), BF ₃ •OEt ₂ (1.1 eq), CH ₂ Cl ₂ , -78°	(71) + (14)	463
		Et ₃ SiH (2 eq), SnCl ₄ (0.1 eq), CH ₂ Cl ₂ , -78°	I (61)	463
		Et ₃ SiH (2.1 eq), (Ph ₃ P) ₃ RhCl (1 mol%), MeC ₆ H ₅ , 50°, 16 h	(91)	471
		Et ₃ SiH (6 eq), BF ₃ (xs), 20°, 6 h	(64)	442
		Et ₃ SiH (xs), BF ₃ •OEt ₂ , 80-95°	I (66-74)	442
		Et ₃ SiH or EtMe ₂ SiH (4 eq), BF ₃ •OEt ₂ (2 mol%), TFA, rt, 0.5 h	(96)	396
		PhSiH ₃ (1.2 eq), Co(dpm) ₂ (5 mol%), rt	(70)	461
		PMHS (1.6 eq), 209 (0.1 mol%), NaOBu- <i>t</i> (3 mol%), MeC ₆ H ₅ , rt, 3 h	(94) dr = 5:1	454

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhSiH_3 (1.3 eq), $\text{Mn}(\text{dpm})_3$ (3 mol%), <i>i</i> -PrOH, DCE	 (99)	448
	1. PhSiH_3 (1.3 eq), $\text{Mn}(\text{dpm})_3$ (3 mol%), <i>i</i> -PrOH, DCE, O_2 2. $\text{P}(\text{OEt})_3$ (1.1 eq)	I (59)	465
	1. PhSiH_3 (1.3 eq), $\text{Mn}(\text{dpm})_3$ (3 mol%), <i>i</i> -PrOH, DCE, O_2 2. $\text{P}(\text{OEt})_3$ (1.1 eq)	 (87)	465
	1. PMHS (0.53 eq), CuCl (10%), $\text{NaOBu-}t$ (5%), (<i>S</i>)- <i>p</i> -Tol-BINAP, MeC_6H_5 , 0° , 2-3 h 2. Allyl bromide, TBAT (1.2 eq)	 (60)	459
	R_3SiH (1.1 eq), $(\text{Ph}_3\text{P})_3\text{RhCl}$	 I +  II I + II I:II (94) 98:2 (95) 85:15 (95) 78:22	435
	R_3Si EtMe ₂ Si PhMe ₂ Si Et ₃ Si		
	Et_3SiH (1.2 eq), TiCl_4 (2.4 eq), CH_2Cl_2 , 0° , 1 h	I (78)	449

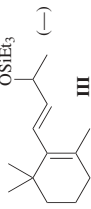
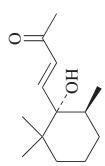
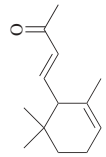
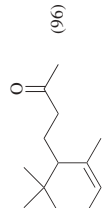
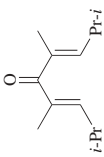
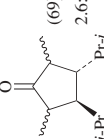

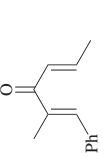
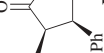


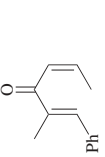

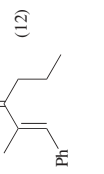
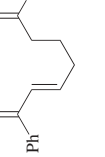
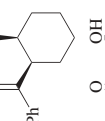

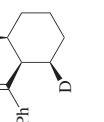
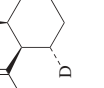
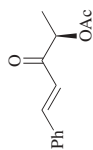
Et ₃ SiH (1.2 eq), (Ph ₃ P) ₃ RhCl, (10-20 mol%), solvent, 50°	I (—) + 	435
Solvent	I:III	
none	64:36	
none	78:22	
C ₆ H ₆ (0.2 M)	86:14	
R ₃ SiH, (Ph ₃ P) ₃ RhCl	I + II (—)	437, 452
R ₃ Si	I:II	
PhMe ₂ Si	91:9	
Et ₃ Si	44:56	
Et ₂ Hsi	0:100	
Ph ₂ Hsi	0:100	
Ph ₂ SiH ₂ (2.5 eq), ZnCl ₂ (0.35 eq), (Ph ₃ P) ₄ Pd (0.019 eq), CHCl ₃ , rt, 2 h	I (96)	436
Ph ₂ SiH ₂ (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), rt, 30 min	I (98), I:II = 100:0	435
PhSiH ₃ (1.5 eq), [(Ph ₃ P)CuH] ₆ (5 mol%), MeC ₆ H ₅ , 47 h	I (96)	447
EtMe ₂ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), C ₆ H ₆ , rt, 15 h	I (94), I:II = 98:2	435
Et ₃ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl (10 mol%), 50°, 2 h	I (96), I:II = 100:0	435
PhSiH ₃ (1.3 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE	I (25)	448
1. PhSiH ₃ (1.3 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE, O ₂ 2. P(OEt) ₃ (1.1 eq)		465

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

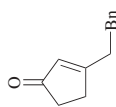
Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH , $(\text{Ph}_3\text{P})_3\text{RhCl}$	 (96)	452
	Et_3SiH (10 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (1.1 eq), CH_2Cl_2 , -78°	 (24) +  (69) 5.7:1 epimer ratio 2.6:1 epimer ratio	463
	Et_3SiH (10 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (1.1 eq), CH_2Cl_2 , -78°	 (18) +  I +  II	463
	Et_3SiH (10 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (1.1 eq), CH_2Cl_2 , -78°	I (19) + II (62)	463
	Et_3SiH (2 eq), SnCl_4 (0.1 eq), CH_2Cl_2 , -78°	I (53) + II (9) +  (12)	463
	PhSiH_3 (120 mol%), $\text{Co}(\text{dpm})_2$ (5 mol%), DCE, rt, 30 min	 (—)	460
	PhSiD_3 (120 mol%), $\text{Co}(\text{dpm})_2$ (5 mol%), DCE, rt, 30 min	 (—) +  (—)	460



PhMe₂SiH, TBAF

(95) 84% selectivity

440



Ph₂MeSiH, TBAF

I (—) 87% selectivity

440

R₃SiH (1.3 eq), **209** (x mol%),

NaOBu-*t* (0.1 mol%), solvent, rt

R ₃ SiH	Solvent	x	Time
PMHS	MeC ₆ H ₅	0.1	1 h
Ph ₂ SiH ₂	MeC ₆ H ₅	0.1	1 h
PMHS	THF	0.1	1 h
Ph ₂ SiH ₂	THF	0.1	1 h
PMHS	MeC ₆ H ₅	0.005	6 h

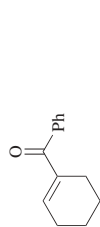
(88)

(87)

(86)

(88)

(86)

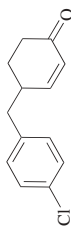


PhSiH₃ (1.3 eq), Mn(dpm)₃ (3 mol%),

i-PrOH, DCE

(50)

448



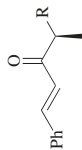
PhSiH₃ (1.5 eq),

[(Ph₃P)CuH]₆ (5 mol%), MeC₆H₅, 6 h

(97)

447

C₁₃₋₁₅



PhMe₂SiH (1.1-1.2 eq),

TBAF (5-10 mol%), HMPA, 0°

OH

R

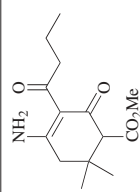
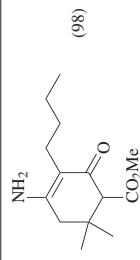
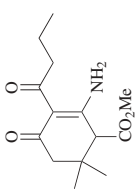
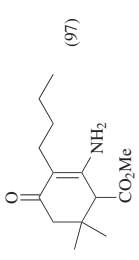
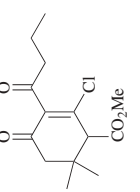
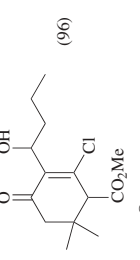
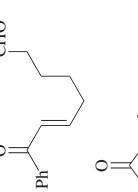
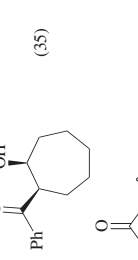
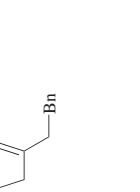
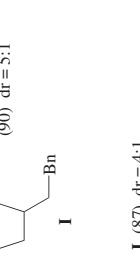


II

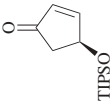
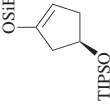
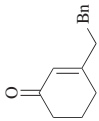
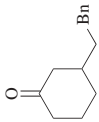
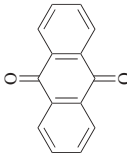
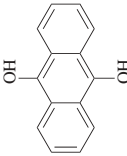
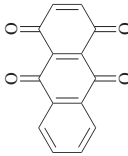
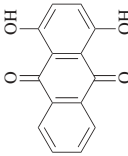
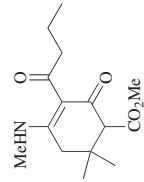
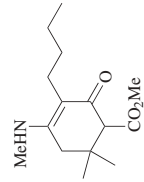
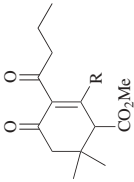
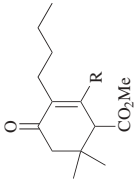
320

R	Time
OAc	12 h
OBu- <i>t</i>	10 h
OTHP	18 h

I + II	I:II
(95)	84:16
(86)	91:9
(77)	87:13

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C14	Et_3SiH or EtMe_2SiH (4 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (2 mol%), TFA, rt, 12 h	 (98)	396
 (97)	Et_3SiH or EtMe_2SiH (4 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (2 mol%), TFA, rt, 12 h	 (97)	396
 (96)	Et_3SiH or EtMe_2SiH (4 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (2 mol%), TFA, rt, 0.5 h	 (96)	396
 (35)	PhSiH_3 (1.2 eq), Co(dpm)_2 (5 mol%), DCE, 35°	 (35)	461
 (90)	PMHS (1.6 eq), 209 (0.1 mol%), $\text{NaOBu-}t$ (0.1 mol%), MeC_6H_5 , rt, 1 h	 (90) dr = 5:1	454
 I	PMHS (3 eq), 209 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mol%), $\text{NaOBu-}t$ (6 mol%), MeC_6H_5 , rt, 1 h	 I (87) dr = 4:1	454

		456
Et_3SiH , $\text{Pt}[(\text{vinylMe}_2\text{Si})_2\text{O}]_2$		
		454
PMHS (1.6 eq), 209 (0.1 mol%), $\text{NaOBu-}t$ (0.1 mol%), MeC_6H_5 , rt, 1 h		
		393
Et_3SiH (5 eq), TFA (20 eq), 60–65°, 20 h	(54)	
		393
Et_3SiH (10 eq), TFA (20 eq), 60–65°, 0.5 h	(99)	
C_{15} 		396
Et_3SiH or EtMe_2SiH (4 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (2 mol%), TFA, rt, 24 h	(98)	
		396
Et_3SiH or EtMe_2SiH (4 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (2 mol%), TFA, rt, 24 h		

R	Time	
	NHMe	OMe
	24 h	8 h
	(98)	(98)

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

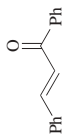
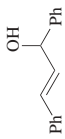
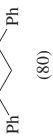
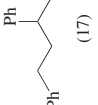
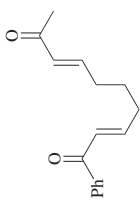
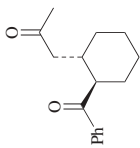
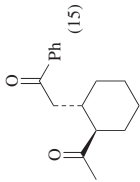
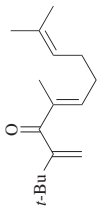
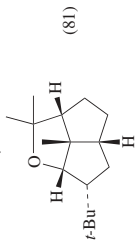
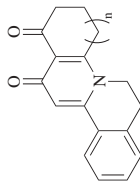
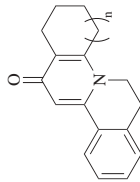
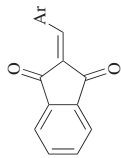
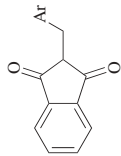




Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
			
C ₁₅			
	Ph ₂ SiH ₂ (0.5 eq), CsF, rt, 30 min	 I + II (95), I:II = 95:5 II	319
	Et ₃ SiH (3 eq), TFA (6 eq), CHCl ₃ , 60°, 7 h	 (80) +  (17)	434
	Et ₃ SiH (1.1 eq), (Ph ₃ P) ₃ RhCl, C ₆ H ₆ , rt, 15 h	II (—)	435
	Ph ₂ SiH ₂ (1.1 eq), (Ph ₃ P) ₃ RhCl, 0° to rt, 6 h	II (—)	435
	PhSiH ₃ (1.1 eq), (Ph ₃ P) ₃ RhCl, 0° to rt, 6 h	II (—)	435
	PhMe ₂ SiH (2 eq), DMA, (Ph ₃ P) ₃ CuF•2 EtOH (1 eq)	II (98)	446
	PhMe ₂ SiH (2 eq), (Ph ₃ P) ₃ CuF•2 EtOH (1.0 eq), DMA, 0° to rt, 3 h	II (98)	444
	PhMe ₂ SiH (1.2 eq), CuCl (20 mol%), PPh ₃ (20 mol%), TBAF (10 mol%), DMA, 0° to rt, 1 h	II (25)	444
	PhMe ₂ SiH (1.2 eq), CuCl (110 mol%), PPh ₃ (110 mol%), TBAF (100 mol%), DMA, 0° to rt, 2 h	II (94)	444
	Ph ₂ SiH ₂ (2.3 eq), CsF (1 eq), 0°, 1 h	I (95) + II (5)	83

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.														
<p>C₁₆</p> 	PhSiH ₃ (2.4 eq), Co(dpm) ₂ (5 mol%), 70°	 (47) +  (15)	461														
	Et ₃ SiH (10 eq), BF ₃ •OEt ₂ (1.1 eq), CH ₂ Cl ₂ , -78°	 (81)	463														
<p>C₁₆₋₁₇</p> 	Et ₃ SiH, BF ₃ •OEt ₂ , TFA, rt, 24 h	 <table data-bbox="526 510 607 597"><tr><td>n</td><td></td></tr><tr><td>0</td><td>(93)</td></tr><tr><td>1</td><td>(62)</td></tr></table>	n		0	(93)	1	(62)	441								
n																	
0	(93)																
1	(62)																
<p>C₁₆₋₁₈</p> 	Et ₃ SiH (5 eq), TFA (10 eq), CCl ₄ , 50-55° <table data-bbox="785 1187 967 1300"><tr><th>Ar</th><th>Time</th></tr><tr><td>Ph</td><td>7 h</td></tr><tr><td>4-MeC₆H₄</td><td>8 h</td></tr><tr><td>4-EtC₆H₄</td><td>7 h</td></tr><tr><td>2-MeC₆H₄</td><td>20 h</td></tr><tr><td>4-MeOC₆H₄</td><td>9 h</td></tr><tr><td>4-ClC₆H₄</td><td>9 h</td></tr></table>	Ar	Time	Ph	7 h	4-MeC ₆ H ₄	8 h	4-EtC ₆ H ₄	7 h	2-MeC ₆ H ₄	20 h	4-MeOC ₆ H ₄	9 h	4-ClC ₆ H ₄	9 h	 (54)  (74)  (53)  (68)  (67) (78)	266
Ar	Time																
Ph	7 h																
4-MeC ₆ H ₄	8 h																
4-EtC ₆ H ₄	7 h																
2-MeC ₆ H ₄	20 h																
4-MeOC ₆ H ₄	9 h																
4-ClC ₆ H ₄	9 h																

C ₁₆₋₁₉		Et ₃ SiH, BF ₃ •OEt ₂ , TFA, rt, 24 h		441
C ₁₆₋₂₃		PhSiH ₃ (120 mol%), Co(dpm) ₂ (5 mol%), DCE, rt, 30 min		460
C ₁₇		Et ₃ SiH (6 eq), TFA (10 eq), CCl ₄ , 50°, 6 h		393
C ₁₇		1. PhMe ₂ SiH (2 eq), (Ph ₃ P) ₃ CuP*2 EtOH, DMA, 0°, 0.5 h 2. Enone, 0° to rt, 2 h		444
C ₁₇		PhMe ₂ SiH, CuCl (25 mol%), PPh ₃ (25 mol%), TBAF (20 mol%), DMA, 0° to rt, 1.5 h		444
C ₁₇		PhSiH ₃ (2.4 eq), Co(dpm) ₂ (5 mol%), 50°		461

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₇</p>	<p>PhSiH₃ (240 mol%), Co(dpm)₂ (5 mol%), DCE, rt, 30 min</p>	<p>(65)</p> <p>+</p> <p>(2)</p>	460
<p>C₁₈</p>	<p>Et₃SiH or EtMe₂SiH (4 eq), BF₃•OEt₂ (2 mol%), TFA, rt</p>	<p>R</p> <p>Time</p> <p>8 h (98)</p> <p>24 h (94)</p>	396
	<p>Et₃SiH or EtMe₂SiH (4 eq), BF₃•OEt₂ (2 mol%), TFA, rt, 12 h</p>	<p>(99)</p>	396
	<p>Et₃SiH or EtMe₂SiH (4 eq), BF₃•OEt₂ (2 mol%), TFA, rt, 12 h</p>	<p>(98)</p>	396
	<p>Et₃SiH, TFA, CH₂Cl₂, 42 h</p>	<p>(60) +</p> <p>(40)</p>	242

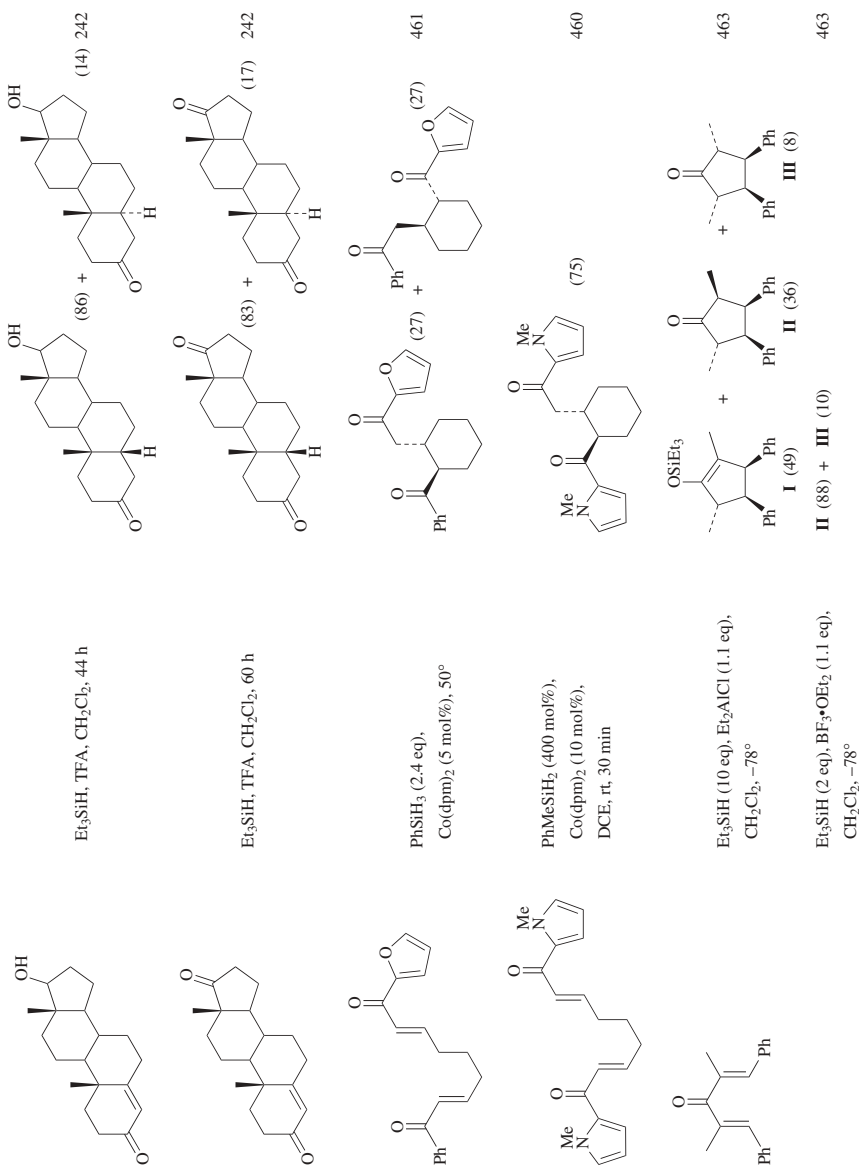
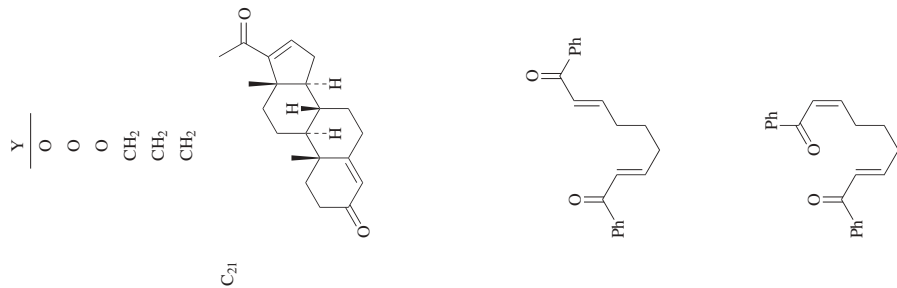


TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

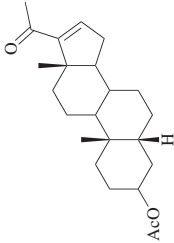
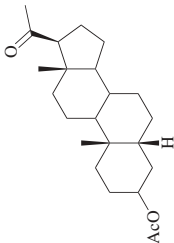
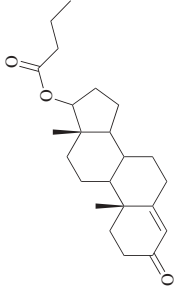
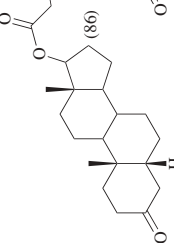
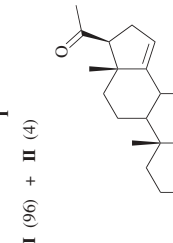
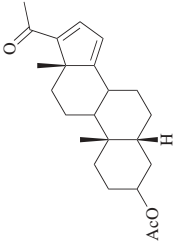
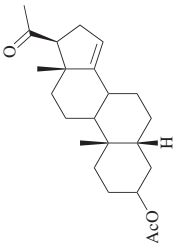
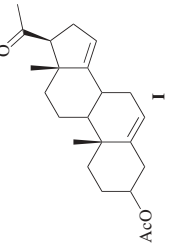
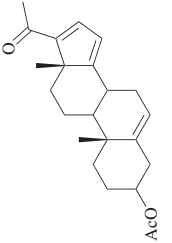
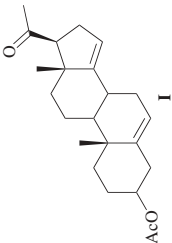
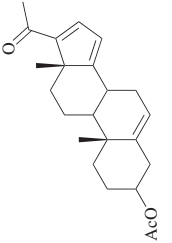
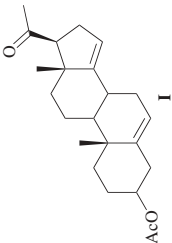
Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₉</p>	<p>Ph₂SiH₂ (1.3 eq), (Ph₃P)₄RhH (0.5 mol%), CH₂Cl₂, rt, 12 h</p>	<p>(56)</p>	374
<p>C₂₀</p>	<p>PhSiH₃ (1.3 eq), Mn(dpm)₃ (3 mol%), <i>i</i>-PrOH, DCE</p>	<p>(100)</p>	448
	<p>PhSiH₃ (2.4 eq), Co(dpm)₂ (5 mol%), 50°</p>	<p>(62)</p>	461
	<p>PhSiH₃ (2.4 eq), Co(dpm)₂ (5 mol%), 50°</p>	<p>(63)</p>	461
<p>C₂₀₋₂₁</p>	<p>R₃SiH (x eq), Co(dpm)₂ (y eq), DDCE, 50°</p>	<p>I + II</p>	462



R ₃ Si	x	y	I	II
PhH ₂ Si	1.2	0.05	(16)	(31)
PhH ₂ Si	2.4	0.05	(—)	(63)
PhMeHSi	4.0	0.10	(69)	(9)
PhH ₂ Si	1.2	0.05	(38)	(41)
PhH ₂ Si	2.4	0.05	(—)	(73)
PhMeHSi	4.0	0.10	(72)	(11)

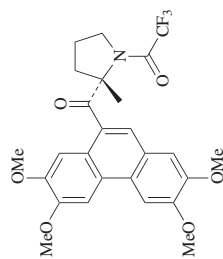
PhSiH ₃ (1.3 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE	<p>(99)</p>	448
1. PhSiH ₃ (1.3 eq), Mn(dpm) ₃ (3 mol%), <i>i</i> -PrOH, DCE, O ₂ 2. P(OEt) ₃ (1.1 eq)	<p>(85)</p>	465
PhSiH ₃ (240 mol%), Co(dpm) ₂ (5 mol%), DCE, rt, 30 min	<p>(70)</p>	460
PhMeSiH ₂ (400 mol%), Co(dpm) ₂ (10 mol%), DCE, rt, 30 min	<p>I (11) + II (72)</p>	460
PhSiH ₃ (120 mol%), Co(dpm) ₂ (5 mol%), DCE rt, 30 min	<p>II (—)</p>	460

TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

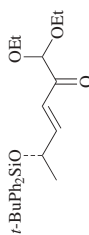
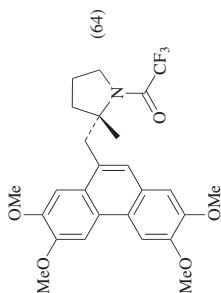
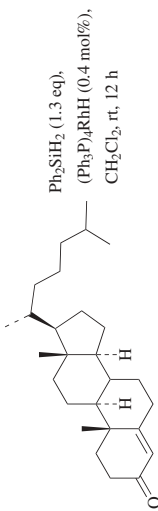
Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (1.2 eq), TiCl_4 (2.4 eq), CH_2Cl_2 , rt, 0.5 h	 (80)	449
	Et_3SiH , TFA, CH_2Cl_2 , 48 h	 (86) +  (14)	242
	Et_3SiH , TFA, 30 h	 I (96) +  II (4)	242
	Et_3SiH (1.2 eq), TiCl_4 (2.4 eq), CH_2Cl_2 , rt, 1 h	 (70-80)	449
	Et_3SiH (1.2 eq), TiCl_4 (2.4 eq), CH_2Cl_2 , rt, 1 h	 (76)	449

$R_3SiH, H_2PtCl_6, MeC_6H_5$

R_3Si	Temp	Time
Et_3Si	150°	5 h
$(n-Pr)_3Si$	160°	7 h
$MeCl_2Si$	60°	0.5 h
Me_2ClSi	60°	0.5 h
$Et_2(EtO)Si$	60°	0.6 h
$Me(EtO)_2Si$	rt	0.4 h
$HMe_2SiOSiMe_2$	rt	0.5 h
$[-(H)(Me)SiO-]_4$	60°	—

C₂₆
 Et_3SiH (3.95 eq), $BF_3 \cdot OEt_2$ (19.8 eq),
 CH_2Cl_2 , rt, 48 h

443

C₂₇

(76)

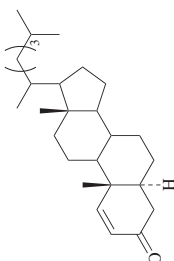
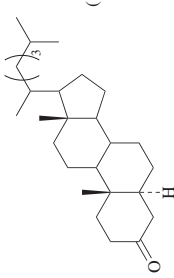
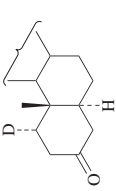
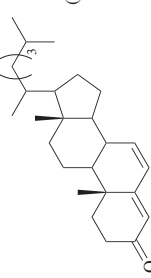
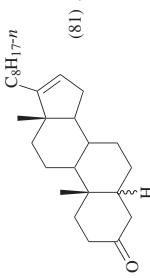
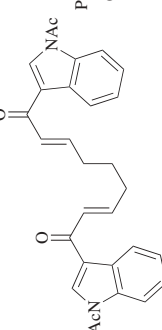
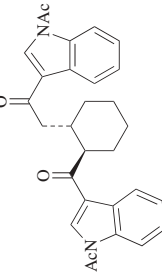
374

 Et_3SiH , $(Ph_3P)_3RhCl$


761



TABLE 16. ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Unsaturated Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₇	<p>Ph₂SiH₂ (1.6 eq), ZnCl₂ (0.5 eq), (Ph₃P)₄Pd (0.03 eq), CHCl₃, rt, 1 h</p>	 (100)	436, 457
 (92)	<p>Ph₂SiD₂ (4 eq), ZnCl₂ (4 eq), (Ph₃P)₄Pd (7.2 mol%), CHCl₃, rt, 1 h</p>		436
 (71)	<p>Ph₂SiH₂ (1.6 eq), ZnCl₂ (0.90 eq), (Ph₃P)₄Pd (0.067 eq), CHCl₃, rt, 1 h</p>		436
 (81) 5 α :5 β = 3:1	<p>Et₃SiH (1.2 eq), TiCl₄ (2.4 eq), CH₂Cl₂, rt, 10 min</p>		449
 C ₂₉	<p>PhSiH₃ (2.4 eq), Co(dppm)₂ (5 mol%), 50°</p>	 (68)	461

^a The yield was determined by NMR analysis.

TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS

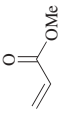
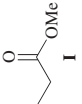
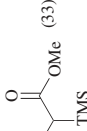
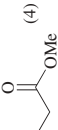
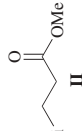
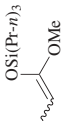


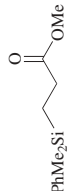
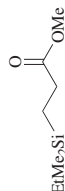
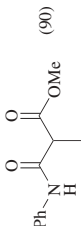
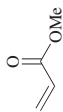
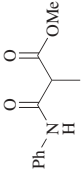
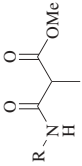
Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	Cl_3SiH (2 eq), CoCl_2 (0.175 eq), CD_3CN , DMI (0.5 eq), 70° , 5 h	 I (96)	451
	PMHS-Pd nanocomposite, C_6H_6 , rt, 4 h	I (96)	219
	TMSH , H_2PtCl_6 (0.5 mol%)	I (22) +  (33) +  (4)	467
	Et_3SiH , H_2PtCl_6 (0.5 mol%)	I (42) +  (26) II	467
	$(n\text{-Pr})_3\text{SiH}$, $(\text{Ph}_3\text{P})_3\text{RhCl}$ (0.5 mol%), 100° , 1 min	 (31.6) +  (38.9)	467
	Et_3SiH , $(\text{Ph}_3\text{P})_3\text{RhCl}$ (0.1 mol%), C_6H_6 , 60° , 1 h	II (54) +  (80)	466
	PhMe_2SiH , $(\text{Ph}_3\text{P})_3\text{RhCl}$ (0.1 mol%), C_6H_6 , 60° , 12 h	 (78)	466
	EtMe_2SiH , $(\text{Ph}_3\text{P})_3\text{RhCl}$ (0.1 mol%), C_6H_6 , 80° , 1 h	 (90)	466
	Et_2MeSiH (1 eq), PhNCO (0.5 eq), $[\text{Rh}(\text{cod})\{\text{P}(\text{OPh})_3\}_2\text{OTf}$ (1 mol%), CH_2Cl_2 , 45° , 3 h	 (90)	475

TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	Et_3MeSiH (1 eq), catalyst (1 mol%), PhNCO (0.5 eq), CH_2Cl_2 , rt Catalyst		475
	Time		
	$[\text{Rh}(\text{cod})][\text{P}(\text{OPh})_3]_2\text{IOTf}$ 21 h	(86)	
	$[\text{Rh}(\text{cod})][\text{P}(\text{OPh})_3]_2\text{IOTf}$ 3 h	(90)	
	$[\text{Rh}(\text{cod})][\text{P}(\text{Ph})_3]_2\text{IOTf}$ 14 h	(95)	
	$[\text{Rh}(\text{cod})][\text{P}(\text{Ph}_2\text{Me})_2\text{IOTf}$ 10 h	(89)	
	$[\text{Rh}(\text{cod})](\text{dppb})\text{IOTf}$ 47 h	(68)	
	$\text{Rh}_4(\text{CO})_{12}$ 47 h	(79)	
	None 68 h	(0)	
	Et_3MeSiH (1 eq), RNCO (0.5 eq), $[\text{Rh}(\text{cod})][\text{P}(\text{OPh})_3]_2\text{IOTf}$ (1 mol%), CH_2Cl_2 , 45°		475
	R		
	Time		
	Ph 3 h	(90)	
	4- ClC_6H_4 3 h	(93)	
	4- BrC_6H_4 13 h	(96)	
	4- MeOC_6H_4 5 h	(73)	
	4- MeC_6H_4 15 h	(96)	
	3- MeC_6H_4 13 h	(96)	
	2- MeC_6H_4 13 h	(86)	
	2- ClC_6H_4 12 h	(94)	
	1- C_{10}H_7 6 h	(99)	
	2- $\text{C}_4\text{H}_3\text{O}$ 4 h	(85)	
	<i>p</i> -Ts 12 h	(82)	
	Bz 14 h	(82)	
	Bn 15 h	(45)	
	<i>c</i> - C_3H_5 61 h	(43)	
	<i>c</i> - C_6H_{11} 24 h	(0)	

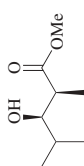
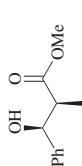
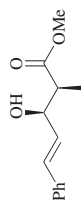
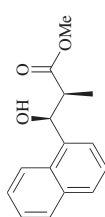
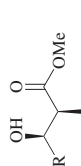
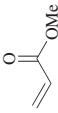
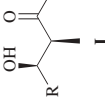


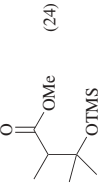
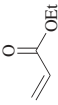
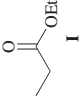


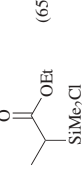
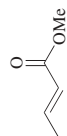
Cl_3MeSiH , $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mol%), Me-DuPHOS (5.5 mol%), $i\text{-PrCHO}$, CH_2Cl_2 , rt, 16 h	 (15) syn:anti = 15:1	762																					
Cl_3MeSiH , $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mol%), Me-DuPHOS (5.5 mol%), PhCHO , CH_2Cl_2 , rt, 16 h	 (69) syn:anti = 23:1	762																					
Cl_3MeSiH , $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mol%), Me-DuPHOS (5.5 mol%), $(E)\text{-PhCH=CHCHO}$, CH_2Cl_2 , rt, 16 h	 (41) syn:anti = >20:1	762																					
Cl_3MeSiH , $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mol%), Me-DuPHOS (5.5 mol%), 1-naphthaldehyde , CH_2Cl_2 , rt, 16 h	 (82) syn:anti = 10:1	762																					
Et_3MeSiH , $[\text{Ir}(\text{cod})\text{Cl}]_2$ (2.5 mol%), RCHO , 97 (7.5 mol%), rt, 24 h	 <div> <div> <div>I</div> <div>II</div> </div> <div> <div>I + II</div> <div>er of I</div> </div> </div> <table> <tr> <td>R</td> <td>I + II</td> <td>er of I</td> </tr> <tr> <td>Ph</td> <td>(68)</td> <td>6.6:1 97:3</td> </tr> <tr> <td>BnOCH₂</td> <td>(49)</td> <td>9.9:1 98:2</td> </tr> <tr> <td>TBSOCH₂</td> <td>(47)</td> <td>8.2:1 98:2</td> </tr> <tr> <td>Et</td> <td>(<5)</td> <td>— —</td> </tr> <tr> <td>BnO(CH₂)₂</td> <td>(65)</td> <td>2.7:1 91:9</td> </tr> <tr> <td>(E)-PhCH=CH</td> <td>(0)</td> <td>— —</td> </tr> </table>	R	I + II	er of I	Ph	(68)	6.6:1 97:3	BnOCH ₂	(49)	9.9:1 98:2	TBSOCH ₂	(47)	8.2:1 98:2	Et	(<5)	— —	BnO(CH ₂) ₂	(65)	2.7:1 91:9	(E)-PhCH=CH	(0)	— —	601
R	I + II	er of I																					
Ph	(68)	6.6:1 97:3																					
BnOCH ₂	(49)	9.9:1 98:2																					
TBSOCH ₂	(47)	8.2:1 98:2																					
Et	(<5)	— —																					
BnO(CH ₂) ₂	(65)	2.7:1 91:9																					
(E)-PhCH=CH	(0)	— —																					

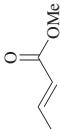
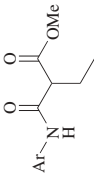
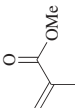

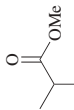
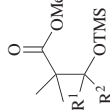
TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	1. $PhSiH_3$ (2 eq), $Co(dpm)_2$ (0.05 mol%), $RCHO$, DCE, 20° 2. H_3O^+	   I + II I:II III (80) 50:50 (10) (62) 50:50 (14)	475
	R $(E)-PhCH=CH$ 20 h $BnCH_2$ 20 h		
	$TMSH$ (1.3 eq), $RhCl_3 \cdot 3H_2O$ (0.009 mol%), acetone, rt	 (24)	473
C_5 	$PhMe_2SiH$ (2 eq), $CoCl_2$ (0.175 eq), CD_3CN , DMI (0.5 eq), 80° , 10 h	 I (70)	451
	Cl_3SiH (2 eq), $CoCl_2$ (0.175 eq), CD_3CN , DMI (0.5 eq), 70° , 5 h		451
	$PhMe_2SiH$, $(Ph_3P)_3RhCl$, 80° , 2 h	 (85)	466
	$EtMe_2SiH$, $(Ph_3P)_3RhCl$, reflux, 12 h	 (83)	466
	$ClMe_2SiH$, $(Ph_3P)_3RhCl$, 70° , 12 h	 (65)	466



<p> Ph_2SiD_2 (1.2 eq), ZnCl_2 (1.74 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (0.02 eq), PPh_3 (0.09 eq), rt, 72 h </p>	<p>(90)</p>	436
<p> 1. TMSh, H_2PtCl_6 (0.5 mol%), 60°, 3 h 2. MeOH, rt </p>	<p>(28) + (54) → (17)</p>	467
<p> TMSh (1.3 eq), $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$ (0.009 mol%), acetone, rt </p>	<p>(89)</p>	473

TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.															
	Et_2MeSiH (1 eq), ArNCO (0.5 eq), $[\text{Rh}(\text{cod})\{\text{P}(\text{OPh})_3\}_2]\text{OTf}$ (1 mol%), CH_2Cl_2 , 45°		475															
	Ar	Time																
	Ph	13 h	(88)															
	4- ClC_6H_4	4 h	(87)															
	4- BrC_6H_4	13 h	(80)															
	4- MeOC_6H_4	14 h	(91)															
	4- MeC_6H_4	12 h	(92)															
	3- MeC_6H_4	14 h	(95)															
	2- MeC_6H_4	14 h	(84)															
	2- ClC_6H_4	5 h	(95)															
	1- C_{10}H_7	15 h	(83)															
	2- $\text{C}_4\text{H}_3\text{O}$	4 h	(53)															
	<i>p</i> -Ts	12 h	(61)															
	Et_2MeSiH (1 eq), PhNCO (0.5 eq), $[\text{Rh}(\text{cod})\{\text{P}(\text{OPh})_3\}_2]\text{OTf}$ (1 mol%), CH_2Cl_2 , 80° , 24 h		475															
	PhSiH_3 (1.3–1.5 eq), $\text{Mo}(\text{CO})_6$ (3–5 mol%), THF, reflux, 20 h		450															
	TMSh (1.3 eq), $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$ (0.009 mol%), $\text{R}^1\text{C}(\text{R}^2)=$, rt		473															
		<table><tr><th>R¹</th><th>R²</th><th></th></tr><tr><td>Me</td><td>Me</td><td>(95)</td></tr><tr><td>Et</td><td>Me</td><td>(91)</td></tr><tr><td>—CH₂CH(Me)(CH₂)₃—</td><td></td><td>(66)</td></tr><tr><td>Me</td><td>H</td><td>(78)</td></tr></table>	R ¹	R ²		Me	Me	(95)	Et	Me	(91)	—CH ₂ CH(Me)(CH ₂) ₃ —		(66)	Me	H	(78)	
R ¹	R ²																	
Me	Me	(95)																
Et	Me	(91)																
—CH ₂ CH(Me)(CH ₂) ₃ —		(66)																
Me	H	(78)																

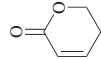
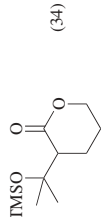
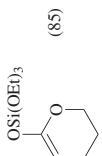

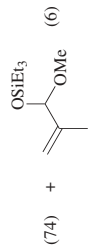
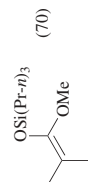
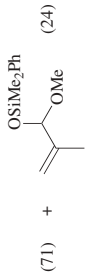
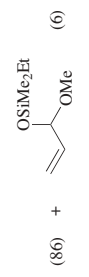
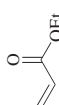
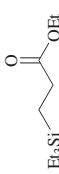
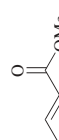
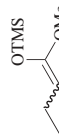
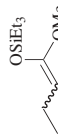
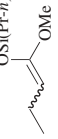
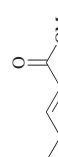

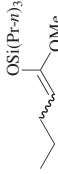
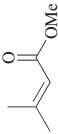
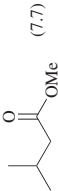
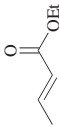
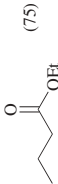
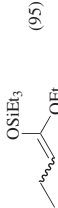
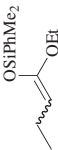
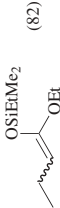
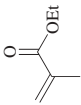
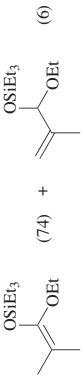
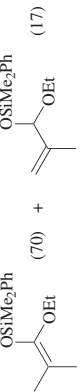
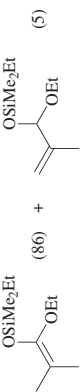
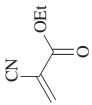
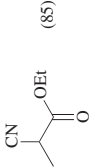
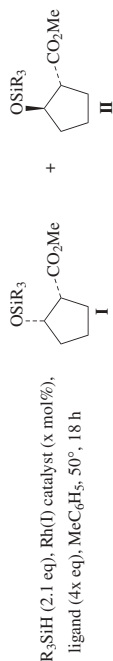
		473
TMSH (1.3 eq), RhCl ₃ ·3H ₂ O (0.009 mol%), acetone, rt	(34)	
(EtO) ₃ SiH (1.1 eq), (P h ₃ P) ₄ RhH (0.3 mol%), CH ₂ Cl ₂ , rt, 12 h		374
(EtO) ₃ SiH (1.1 eq), (P h ₃ P) ₄ RhH (0.3 mol%), CH ₂ Cl ₂ , rt, 1.5 h		374
Et ₃ SiH, (Ph ₃ P) ₃ RhCl, C ₆ H ₆ , 70°, 2 h		466
(<i>n</i> -Pr) ₃ SiH, (Ph ₃ P) ₃ RhCl (0.5 mol%), 100°, 1 min		467
PhMe ₂ SiH, (Ph ₃ P) ₃ RhCl, 60°, 2 h		466
EtMe ₂ SiH, (Ph ₃ P) ₃ RhCl, C ₆ H ₆ , 70°, 12 h		466

TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	Et_3SiH , $(Ph_3P)_3RhCl$, C_6H_6 , 70° , 3 h		466
	1. $TMSH$, $(Ph_3P)_3RhCl$ (0.5 mol %), 60° , 10 min 2. $MeOH$, rt		467
	1. Et_3SiH , $(Ph_3P)_3RhCl$ (0.5 mol %), 100° , 1 min 2. $MeOH$, rt		467
	1. $(n-Pr)_3SiH$, $(Ph_3P)_3RhCl$ (0.5 mol %), 100° , 1 min 2. $MeOH$, rt		467
C_6 	$TMSH$, H_2PtCl_6 (0.5 mol %)		467
	$n-Pr_3SiH$, $(Ph_3P)_3RhCl$ (0.5 mol %), 100° , 1 min		467

		PhSiH ₃ (1.01 eq), Ni, PPh ₃ (0.02 eq)	438
		PhSiH ₃ (1.3-1.5 eq), Mo(CO) ₆ (3-5 mol%), THF, reflux, 11.5 h	450
	I (90)	Ph ₃ SiH ₂ (2.4 eq), ZnCl ₂ (1.7 eq), (Ph ₃ P) ₄ Pd (0.02 eq), PPh ₃ (0.09 eq), CHCl ₃ , rt, 48 h	436
		Et ₃ SiH, (Ph ₃ P) ₃ RhCl, 50°, 1 h	466
		PhMe ₂ SiH, (Ph ₃ P) ₃ RhCl, 50°, 1 h	466
		EtMe ₂ SiH, (Ph ₃ P) ₃ RhCl, 80°, 1 h	466
		Et ₃ SiH, (Ph ₃ P) ₃ RhCl, C ₆ H ₆ , 80°, 2 h	466
		PhMe ₂ SiH, (Ph ₃ P) ₃ RhCl, 65°, 1 h	466
		EtMe ₂ SiH, (Ph ₃ P) ₃ RhCl, 40°, 16 h	466
		Et ₃ SiH (1 eq), TFA (3 eq), 0°, <5 min	236

Ligand	I + II	I:II
(<i>c</i> -C ₆ H ₁₁) ₃ P	(79)	2.5:1
DIPHOS	(78)	3.3:1
(<i>p</i> -tol) ₃ P	(27)	1::2
(<i>p</i> -tol) ₃ P	(53)	2:1
(PMP) ₃ P	(61)	1:1.6
(PMP) ₃ P	(51)	2:1



472

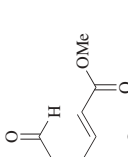
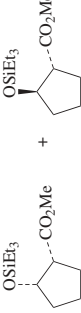

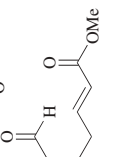


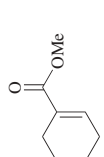
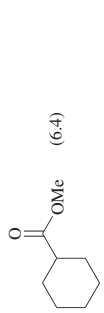
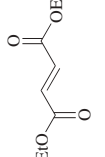
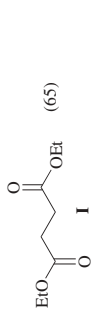
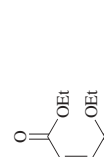
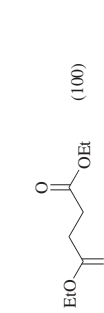
R ₃ Si	Catalyst	x	Ligand	I + II	I:II
Et ₃ Si	(Ph ₃ P) ₃ RhCl	1.0	none	(81)	3.0
PhMe ₂ Si	(Ph ₃ P) ₃ RhCl	1.0	none	(62)	2.4
Ph ₂ MeSi	(Ph ₃ P) ₃ RhCl	1.0	none	(49)	2.8
Ph ₃ Si	(Ph ₃ P) ₃ RhCl	1.0	none	(42)	1.5
Et ₃ Si	[(<i>c</i> -C ₈ H ₁₄) ₂ RhCl] ₂	2.5	(<i>c</i> -C ₆ H ₁₁) ₃ P	(79)	2.5
Et ₃ Si	[(<i>c</i> -C ₈ H ₁₄) ₂ RhCl] ₂	2.5	dppe	(78)	3.3
Et ₃ Si	[(<i>c</i> -C ₈ H ₁₄) ₂ RhCl] ₂	2.5	(<i>p</i> -tol) ₃ P	(27)	0.5
Et ₃ Si	[(<i>c</i> -C ₈ H ₁₄) ₂ RhCl] ₂	2.5	(PMP) ₃ P	(61)	0.6
Et ₃ Si	(Ph ₃ P) ₄ RhH	1.0	none	(81)	0.5

R_3SiH (2.1 eq), (Ph₃P)₃RhCl (1 mol%),
 MeC_6H_5 , 50°, 18 h

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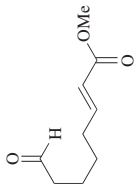
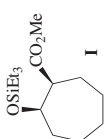
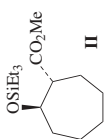
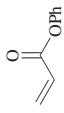
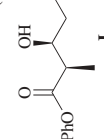
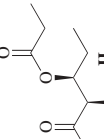
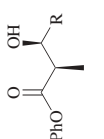
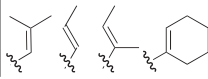
R ₃ Si	I + II	I:II
Et ₃ Si	(81)	2.0:1
PhMe ₂ Si	(62)	2.4:1
Ph ₂ MeSi	(49)	2.8:1
Ph ₃ Si	(42)	1.5:1

TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇ 	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₄ RhH (1 mol %), MeC ₆ H ₅ , 50°, 18 h	 I +  II I + II (81), I:II = 1:11	471
C ₈ 	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₃ RhCl (1 mol %), MeC ₆ H ₅ , 50°, 16 h	 I +  II I + II (66), I:II = 1:4.6	471
	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₄ RhH (1 mol %), MeC ₆ H ₅ , 50°, 16 h	I + II (65), I:II = 1:3	471
	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₃ RhCl (3 mol %), MeC ₆ H ₅ , 70°	II (29)	472
	PhSiH ₃ (1.01 eq), Ni, PPh ₃ (0.02 eq)	 (6.4)	438
	PhMe ₂ SiH (1.2 eq), CuCl (110 mol %), PPh ₃ (110 mol %), TBAF (100 mol %), DMA, 0° to rt, 2 h	 I (65)	444
	PhSiH ₃ (1.3-1.5 eq), Mo(CO) ₆ (3-5 mol %), THF, reflux, 4.5 h	I (100)	450
	PhSiH ₃ (1.3-1.5 eq), Mo(CO) ₆ (3-5 mol %), THF, reflux, 10 h	 (100)	450

C ₈ -13			R	468
	Et ₃ SiH (3.15 eq), TFA (19.5 eq), CH ₂ Cl ₂ , rt, 1.5 h		EtO (83) Me ₂ N (75) Ph (60) BnS (89)	
C ₉			(16) dr = 3:1	474
	MeCl ₂ SiH, [Rh(cod)Cl] ₂ (2.5 mol%), Me-DuPHOS (5 mol %), C ₆ H ₆ , rt, 4 h			
	R ₃ SiH, [Rh(cod)Cl] ₂ (2.5 mol%), Me-DuPHOS (5 mol %), C ₆ H ₆ , rt		dr	474
			(74) 11:1 (8) 4.3:1 (0) — (47) 21:1 (47) >25:1 (9) 10:1 (0) — (0) —	
	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₄ RhCl (1 mol%), MeC ₆ H ₅ , 50°, 16 h			471
	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₄ RhH (1 mol%), MeC ₆ H ₅ , 50°, 16 h			471

TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.																
	<p>Et₃SiH (2.1 eq), (Ph₃P)₄RhH (1 mol%), MeC₆H₅, 50°, 16 h</p>	  <p>I + II (68), I:II = 2.5:1</p>	471																
	<p>1. EtMe₂SiH (1.0 eq), [Rh(cod)Cl]₂ (2.5 mol%), CH₃CH₂CHO (0.83 eq), (<i>R</i>)-BINAP (6.5 mol%), rt, 24 h 2. H₃O⁺</p>	  <p>I + II (46) dr = 4.6:1, er = 94:6</p>	470																
	<p>1. R₃SiH (0.5 eq), [Rh(cod){(<i>R</i>)-BINAP}] BF₄ (5 mol%), CH₃CH₂CHO (2.0 eq) 2. H₃O⁺</p>	<p>I + II</p>	470																
	<p>R₃Si</p>	<table> <tr> <th>I</th><th>II</th><th>er I</th><th>er II</th></tr> <tr> <td>(23)</td><td>(42)</td><td>91:9</td><td>91:9</td></tr> <tr> <td>(18)</td><td>(48)</td><td>90:10</td><td>90:10</td></tr> <tr> <td>(0)</td><td>(29)</td><td>—</td><td>89:11</td></tr> </table>	I	II	er I	er II	(23)	(42)	91:9	91:9	(18)	(48)	90:10	90:10	(0)	(29)	—	89:11	
I	II	er I	er II																
(23)	(42)	91:9	91:9																
(18)	(48)	90:10	90:10																
(0)	(29)	—	89:11																
	<p>Et₂MeSi PhMe₂Si (EtO)Me₂Si</p>																		
	<p>Et₂MeSiH (0.35 eq), [Rh(cod){(<i>R</i>)-BINAP}] BF₄ (5 mol%), RCHO (0.2 eq), rt, 12 h</p>		470																
	<p>R</p>																		
		<p>(86) syn:anti = 6:1, ee syn = 83% (54) syn:anti = 6:1, ee syn = 71% (90) syn:anti = 3:1, ee syn = 75% (73) syn:anti = 7:1, ee syn = 81%</p>																	

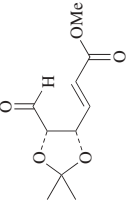
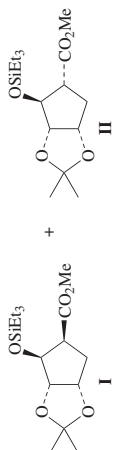
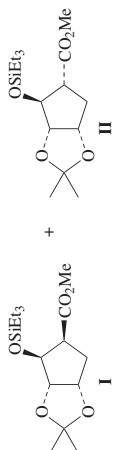
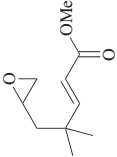
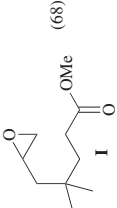
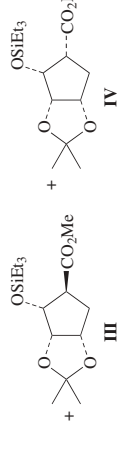
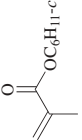


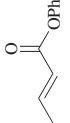
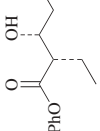

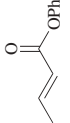
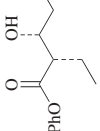

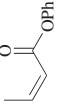
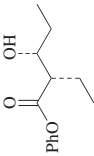
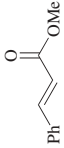
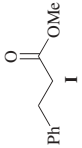
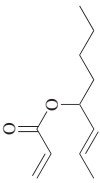
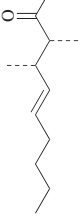
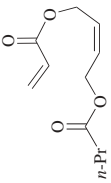
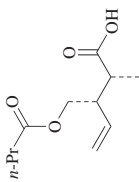
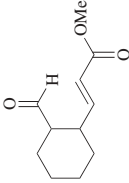
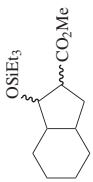
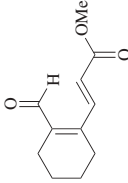
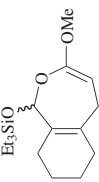
			471
	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₃ RhCl (1 mol%), MeC ₆ H ₅ , 50°, 16 h		
			471
	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₃ RhCl (1 mol%), MeC ₆ H ₅ , 50°, 16 h		
			471
	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₄ RhH (1 mol%), MeC ₆ H ₅ , 50°, 16 h		
			450
	PhSiH ₃ (1.3-1.5 eq), Mo(CO) ₆ (3-5 mol%), THF, reflux, 35 h		
			470
	Et ₃ MeSiH (5 eq), [Rh(cod)Cl] ₂ (5 mol%), (S)-BINAP (6.5 mol%), CH ₃ CH ₂ CHO (0.83 eq), rt, 48 h		

TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

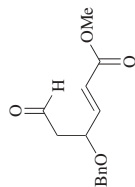
Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3MeSiH (5 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (5 mol%), (<i>S</i>)-BINAP (6.5 mol%), $\text{CH}_3\text{CH}_2\text{CHO}$ (0.83 eq), rt, 48 h	 (52) syn:anti = 3.9:1, ee syn = 88%	470
	Ph_2SiH_2 (1.7 eq), ZnCl_2 (0.76 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (0.02 eq), PPh_3 (0.05 eq), rt, 48 h	 (80)	436
	PhSiH_3 (1.5 eq), $[(\text{Ph}_3\text{P})\text{CuH}]_6$ (5 mol%), MeC_6H_5 , 20 min	 (91) dr > 25:1	447
	MeCl_2SiH , $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mol%), Me-DuPHOS (5 mol%), C_6H_6 , rt, 4 h	 (50) dr = 23:1	474
	Et_3SiH (2.1 eq), $(\text{Ph}_3\text{P})_4\text{RhH}$ (1 mol%), MeC_6H_5 , 50°, 16 h	 (81)	471
	Et_3SiH (2.1 eq), $(\text{Ph}_3\text{P})_4\text{RhH}$ (1 mol%), MeC_6H_5 , 50°, 16 h	 (88)	471

		Et_3SiH (2.1 eq), $(\text{Ph}_3\text{P})_3\text{RhCl}$ (1 mol%), MeC_6H_5 , 50° , 16 h	(61) dr = 1.5:1	471
	I (69) dr = 1:20	Et_3SiH (2.1 eq), $(\text{Ph}_3\text{P})_3\text{RhCl}$ (1 mol%), MeC_6H_5 , 50° , 16 h		471
	(0)	Et_3MeSiH (5 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (5 mol%), (<i>S</i>)-BINAP (6.5 mol%), $\text{CH}_3\text{CH}_2\text{CHO}$ (0.83 eq), rt, 48 h		470
	I	PhMe_2SiH (2 eq), CuCl (x eq), DMI, rt, 5 h	x 1 (96) 0.5 (90) 0.2 (86) 0.1 (0)	445
	I (54)	PhMe_2SiH (1.2 eq), CuCl (20 mol%), PPh_3 (20 mol%), TBAF (10 mol%), DMA, 0° to rt, 4.5 h		444
	I (50)	Cl_3SiH (2 eq), CoCl_2 (0.175 eq), CD_3CN , DMI (0.5 eq), 70° , 5 h		451
	(76) dr > 25:1	MeCl_2SiH , $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mol%), Me-DuPHOS (5 mol%), C_6H_6 , rt, 15 h		474
	(74)	MeCl_2SiH , $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mol%), Me-DuPHOS (5 mol%), C_6H_6 , rt, 15 h		474

C₁₂

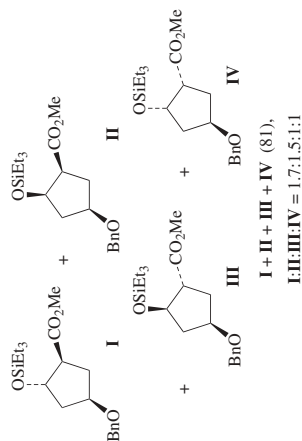
TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂ 	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₃ RhCl (1 mol%), MeC ₆ H ₅ , 50°, 16 h	 + I + II (54), I:II = 2:1	471
	Et ₃ SiH (2.1 eq), (Ph ₃ P) ₃ RhCl (1 mol%), MeC ₆ H ₅ , 50°, 16 h	 (91)	471
	PhSiH ₃ (1.3-1.5 eq), Mo(CO) ₆ (3-5 mol%), THF, reflux, 24 h	 (90)	450
	PMHS (4 eq), 209 (0.3 mol%), NaOBu- <i>t</i> (0.1 mol%), <i>t</i> -BuOH (4 eq), MeC ₆ H ₅ , rt, 1 h	 (91)	454
	PMHS (4 eq), 209 (0.3 mol%), NaOBu- <i>t</i> (1.8 mol%), <i>t</i> -BuOH (4 eq), MeC ₆ H ₅ , rt, 1 h	I (88)	454
C ₁₃ 	PMHS (4 eq), 209 (0.3 mol%), NaOBu- <i>t</i> (0.1 mol%), <i>t</i> -BuOH (4 eq), MeC ₆ H ₅ , rt, 1 h	 (97)	454
	PMHS (12 eq), 209 (2 mol%), NaOBu- <i>t</i> (0.1 mol%), <i>t</i> -BuOH (12 eq), MeC ₆ H ₅ , rt, 4 h	 (93) dr = 1.5:1	454

C₁₄

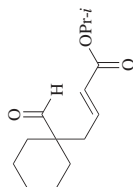
Et₃SiH (2.1 eq), (Ph₃P)₃RhCl (1 mol %),
MePh, 50°, 16 h

471



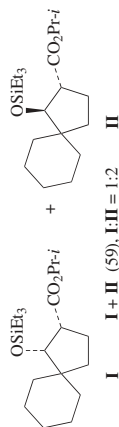
Et₃SiH (2.1 eq), (Ph₃P)₄RhH (1 mol %),
MePh, 50°, 16 h

471



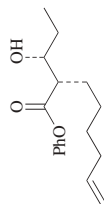
Et₃SiH (2.1 eq), (Ph₃P)₄RhH (1 mol %),
MePh, 50°, 16 h

471

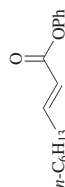


Et₃MeSiH (5 eq), [Rh(cod)Cl]₂ (5 mol %),
(S)-BINAP (6.5 mol %),
CH₃CH₂CHO (0.83 eq), rt, 48 h

470

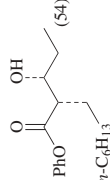


(30) syn:anti = 4.4:1, —% ee syn

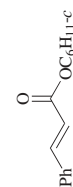
C₁₅

Et₃MeSiH (5 eq), [Rh(cod)Cl]₂ (5 mol %),
(S)-BINAP (6.5 mol %),
CH₃CH₂CHO (0.83 eq), rt, 48 h

470



(54) syn:anti = 4.2:1, 88% ee syn

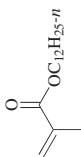
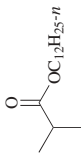
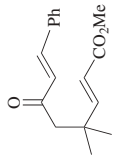
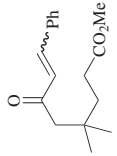

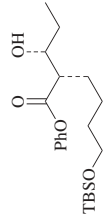

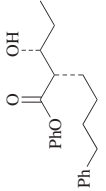
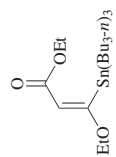
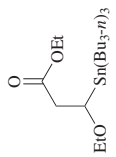


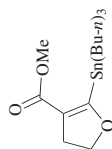
PhSiH₃ (1.3–1.5 eq),
Mo(CO)₆ (3–5 mol %),
THF, reflux, 30 h

450



TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C_{16}</p> 	<p>PhMe₂SiH (4 eq), CuCl (2 eq), DMI, rt, 6 h</p>	<p>(95)</p> 	445
<p>C_{18}</p> 	<p>Et₃SiH (2.1 eq), (Ph₃P)₃RhCl (1 mol%), MeC₆H₅, 50°, 16 h</p>	<p>(74)</p> 	471
	<p>Et₃MeSiH (5 eq), [Rh(cod)Cl]₂ (5 mol%), (<i>S</i>)-BINAP (6.5 mol%), CH₃CH₂CHO (0.83 eq), rt, 48 h</p>	 <p>(53) syn:anti = 3.8:1, 88% ee syn</p>	470
	<p>Et₃MeSiH (5 eq), [Rh(cod)Cl]₂ (5 mol%), (<i>S</i>)-BINAP (6.5 mol%), CH₃CH₂CHO (0.83 eq), rt, 48 h</p>	 <p>(49) syn:anti = 3.9:1, 93% ee syn</p>	470
<p>C_{19}</p> 	<p>Et₃SiH (10 eq), TMSOTf (2 eq), CH₂Cl₂, -78°, 1 h</p>	<p>(72)</p> 	469



R_3SiH (10 eq), acid (2 eq),
 CH_2Cl_2 , -78° , rt, 4 h

R_3Si	Acid
Et_3Si	$BF_3 \cdot OEt_2$
Et_3Si	TFA
Et_3Si	TMSOTf
Et_3Si	HOAc
Ph_3Si	TMSOTf
Ph_3Si	TFA

(71)

(96)

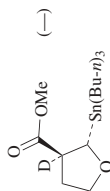
(98)

(l)

(74)

(54)

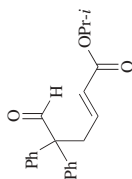
469



(—)

469

C₂₁

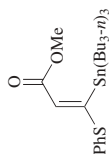


Et_3SiH (2.1 eq), $(Ph_3P)_4RhH$ (1 mol%),
 MePh, 50° , 16 h



471

C₂₂

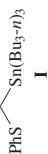


Et_3SiH (10 eq), $BF_3 \cdot OEt_2$ (2 eq),
 CH_2Cl_2 , -78° , 1 h; rt, 5 d

(42)

469

Et_3SiH (10 eq), TMSOTf (2 eq),
 CH_2Cl_2 , -78° , 1 h; 0° , 5 h; rt, 5 d
 Et_3SiH (10 eq), TFA (2 eq),
 CH_2Cl_2 , -78° , 1 h; 0° , 1 h; rt, 4 h



I (24)

469

I (24)

469

TABLE 17. ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

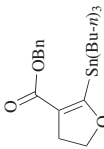
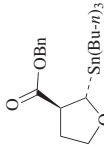
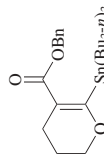
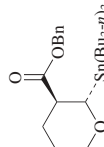
Unsaturated Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₄</p> 	<p>Et₃SiH (10 eq), TMSOTf (2 eq), CH₂Cl₂, -78° to rt, 1 h; 0° 1 h</p>	<p>(61)</p> 	469
<p>C₂₅</p> 	<p>Et₃SiH (10 eq), TFA (2 eq), CH₂Cl₂, -78°, 1 h</p>	<p>(64)</p> 	469

TABLE 18. ORGANOSILANE REDUCTION OF α,β -UNSATURATED AMIDES

Unsaturated Amide	Conditions	Product(s) and Yield(s) (%)	Refs.							
<div>C₃₋₉</div> <div></div>	<p>PhSiH₃ (1.3-1.5 eq), Mo(CO)₆ (3-5 mol%), THF, reflux</p> <table><tr><th>Time</th></tr><tr><td>1 h</td></tr><tr><td>0.3 h</td></tr><tr><td>0.2 h</td></tr><tr><td>0.2 h</td></tr></table>	Time	1 h	0.3 h	0.2 h	0.2 h	<div></div> <div>(80) (100) (100) (95)</div>	450		
Time										
1 h										
0.3 h										
0.2 h										
0.2 h										
<div>C₄₋₁₀</div> <div></div>	<p>PhSiH₃ (1.3-1.5 eq), Mo(CO)₆ (3-5 mol%), THF, reflux</p> <table><tr><th>Time</th></tr><tr><td>1.7 h</td></tr><tr><td>1.3 h</td></tr><tr><td>4 h</td></tr><tr><td>15 h</td></tr></table>	Time	1.7 h	1.3 h	4 h	15 h	<div></div> <div>(100) (100) (70) (80)</div>	450		
Time										
1.7 h										
1.3 h										
4 h										
15 h										
<div>C₅</div> <div></div>	<p>Cl₃SiH (1.3 eq), (Ph₃P)₄Pd, (5 mol%), RCHO, CH₂Cl₂, rt, 45 h</p> <table><tr><th>R</th></tr><tr><td>Ph</td></tr><tr><td>1-C₁₀H₇</td></tr><tr><td>4-MeC₆H₄</td></tr><tr><td>2-C₁₀H₇</td></tr><tr><td>4-O₂NC₆H₄</td></tr><tr><td>4-ClC₆H₄</td></tr></table>	R	Ph	1-C ₁₀ H ₇	4-MeC ₆ H ₄	2-C ₁₀ H ₇	4-O ₂ NC ₆ H ₄	4-ClC ₆ H ₄	<div></div> <div>I + II I:II (87) 32:68 (78) 24:76 (72) 31:69 (93) 30:70 (68) 28:72 (75) 36:64</div>	763
R										
Ph										
1-C ₁₀ H ₇										
4-MeC ₆ H ₄										
2-C ₁₀ H ₇										
4-O ₂ NC ₆ H ₄										
4-ClC ₆ H ₄										

TABLE 18. ORGANOSILANE REDUCTION OF α,β -UNSATURATED AMIDES (Continued)

Unsaturated Amide	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
<div>$C_{3,6}$ </div>	$PhSiH_3$ (2 eq), CoX_2 (0.05 mol%), R^3CHO , $ClCH_2CH_2Cl$, 20°	<div></div> <div></div> <div></div> 478																																									
	<table><tr><th>R^3</th><th>R^2</th><th>Time</th></tr><tr><td>Ph</td><td>H</td><td>2 h</td></tr><tr><td>(<i>E</i>)-PhCH=CH</td><td>H</td><td>4 h</td></tr><tr><td>BnCH₂</td><td>H</td><td>6 h</td></tr><tr><td>Ph</td><td>Me</td><td>3 h</td></tr><tr><td>(<i>E</i>)-PhCH=CH</td><td>Me</td><td>4 h</td></tr><tr><td>Ph</td><td>Me</td><td>5 h</td></tr><tr><td>(<i>E</i>)-PhCH=CH</td><td>Me</td><td>4 h</td></tr></table>	R^3	R^2	Time	Ph	H	2 h	(<i>E</i>)-PhCH=CH	H	4 h	BnCH ₂	H	6 h	Ph	Me	3 h	(<i>E</i>)-PhCH=CH	Me	4 h	Ph	Me	5 h	(<i>E</i>)-PhCH=CH	Me	4 h	<table><tr><th>I + II</th><th>III</th></tr><tr><td>(95)</td><td>80:20 (3)</td></tr><tr><td>(96)</td><td>72:28 (trace)</td></tr><tr><td>(90)</td><td>70:30 (trace)</td></tr><tr><td>(72)</td><td>70:30 (10)</td></tr><tr><td>(68)</td><td>72:28 (12)</td></tr><tr><td>(50)</td><td>— (31)</td></tr><tr><td>(70)</td><td>— (14)</td></tr></table>	I + II	III	(95)	80:20 (3)	(96)	72:28 (trace)	(90)	70:30 (trace)	(72)	70:30 (10)	(68)	72:28 (12)	(50)	— (31)	(70)	— (14)	
R^3	R^2	Time																																									
Ph	H	2 h																																									
(<i>E</i>)-PhCH=CH	H	4 h																																									
BnCH ₂	H	6 h																																									
Ph	Me	3 h																																									
(<i>E</i>)-PhCH=CH	Me	4 h																																									
Ph	Me	5 h																																									
(<i>E</i>)-PhCH=CH	Me	4 h																																									
I + II	III																																										
(95)	80:20 (3)																																										
(96)	72:28 (trace)																																										
(90)	70:30 (trace)																																										
(72)	70:30 (10)																																										
(68)	72:28 (12)																																										
(50)	— (31)																																										
(70)	— (14)																																										
<div>C_{10} </div>	Ph_2SiH_2 (1.5 eq), $ZnCl_2$ (1.0 eq), $(Ph_3P)_4Pd$ (0.011 eq), PPh_3 (0.019 eq), rt, 10 h	<div></div> 78	436																																								
	$PhSiH_3$ (1.3-1.5 eq), $Mo(CO)_6$ (3-5 mol%), THF, reflux, 4 h	<div></div> 80	450																																								
<div>C_{11} </div>	Ph_2SiH_2 (3 eq), $ZnCl_2$ (1.1 eq), $(Ph_3P)_4Pd$ (0.011 eq), PPh_3 (0.019 eq), $CHCl_3$, rt, 10 h	<div></div> 78	436																																								
<div>C_{25} </div>	Et_3SiH (10 eq), $TMSOTf$ (2 eq), CH_2Cl_2 , -78° , 1.5 h	<div></div> 41 + <div></div> (0.5)	469																																								

TABLE 19. ORGANOSILANE REDUCTION OF α,β -UNSATURATED NITRILES

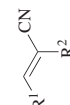
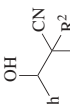










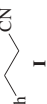





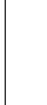







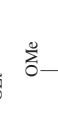



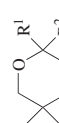




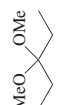
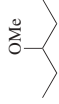
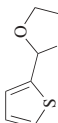

Unsaturated Nitrile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-4} 	$PhSiH_3$ (2 eq), CoX_2 (0.05 mol%), $PhCHO$, $ClCH_2CH_2Cl$	                    	

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₅ </p>	I ₂ SiH ₂ (2 eq), CHCl ₃ , 22°, 30 min	 (100)	358
<p>C₆ </p>	I ₂ SiH ₂ (2 eq), CHCl ₃ , 22°, 30 min	I (99)	358
<p>C₆ </p>	1. I ₂ SiH ₂ (2 eq), CHCl ₃ , 22°, 30 min 2. I ₂	 (100)	358
<p>C₆ </p>	TMSH (1.1 eq), TMSOTf (0.01 eq), CH ₂ Cl ₂ , 0°, 30 min	 OMe (100)	480
<p>C₆₋₈ </p>	I ₂ SiH ₂ (3 eq), CHCl ₃ , 22°, 12 h	 I (100)	358
<p>C₆₋₈ </p>	Et ₃ SiH, TFA, rt	 HO  + CF ₃ O ₂ C  + R ¹ R ² CHO  (—)	764
<p>C₇ </p>	TMSH (1.1 eq), TMSOTf (0.01 eq), CH ₂ Cl ₂ , 0°, 30 min	 OMe (100) ^a	480
<p></p>	Et ₃ SiH, TFA, 55°, 15 h	 OSiEt ₃ (45)	260

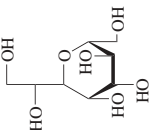
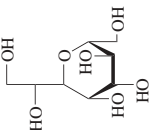
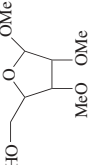
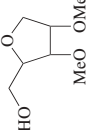
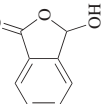
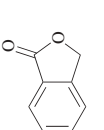

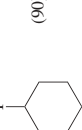

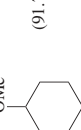

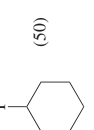

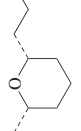

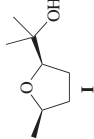
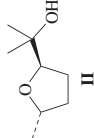
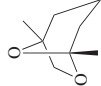
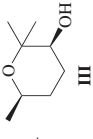
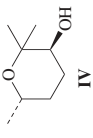

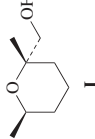
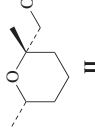

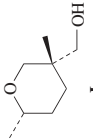
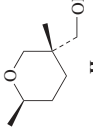


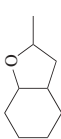
		Et ₃ SiH, TMSOTf, MeCN	518
		Et ₃ SiH (30 eq), BF ₃ •OEt ₂ (30 eq), TFA (12 eq), 0° to rt, 16 h	483
		1. <i>i</i> -Bu ₂ NH, hexanes, MeC ₆ H ₅ , -78° 2. Et ₃ SiH (1.5 eq), BF ₃ •OEt ₂ (1.1 eq), 0°, 10 min	510
		I ₂ SiH ₂ (2 eq), CHCl ₃ , 22°, 2 h	358
		Et ₃ SiH (1.1 eq), Nafion [®] -H, CH ₂ Cl ₂ , reflux, 4 h	335
		I ₂ SiH ₂ (3 eq), CHCl ₃ , 22°, 24 h	358
		Ph ₂ SiH ₂ (1.5 eq), TiCl ₄ (1.2 eq), CH ₂ Cl ₂ , -78°, 15 min	492

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (1.5 eq), TiCl_4 (1.2 eq), CH_2Cl_2 , -78°	  495	
	Ph_2SiH_2 (1.5 eq), TiCl_4 (1.2 eq), CH_2Cl_2 , -78° , 15 min	  $\text{I} + \text{II} + \text{III} + \text{IV}$ (61), $\text{I:II:III:IV} = 42:6:0.8:48$; 7:7.9 495	
	Et_3SiH (1.5 eq), TiCl_4 (1.2 eq), CH_2Cl_2 , -78°	  $\text{I} + \text{II}$ (76), $\text{I:II} = 7:93$ $\text{I} + \text{II}$ (82), $\text{I:II} = 1:99$ 495	
	Et_3SiH (1.2 eq), TiCl_4 (1.2 eq), CH_2Cl_2 , -78° , 15 min	  $\text{I} + \text{II}$ (71), $\text{I:II} = 63:36$ 495	
	Et_3SiH (1.2 eq), SnCl_4 (1.2 eq), CH_2Cl_2 , -78°	$\text{I} + \text{II}$ (72), $\text{I:II} = 76:24$ 495	
	Et_3SiH , HOTf	 $\text{I} + \text{II}$ (51) single diastereomer 499	



TBBSH (1.4 eq), R³OTMS (3 eq),
Sn(OTf)₂, MeCN, -20°, 3-6 h



R ¹	R ²	R ³	
—(CH ₂) ₅ —	H	Bn	(87)
<i>c</i> -C ₆ H ₁₁	H	Bn	(82)
Ph	H	Bn	(87)
Ph	H	<i>n</i> -C ₈ H ₁₇	(86)
Ph	H	allyl	(80)
Ph	H	<i>c</i> -C ₆ H ₁₁	(86)
4-ClC ₆ H ₄	H	Bn	(93)
Ph	Me	Bn	(70)
3-MeOC ₆ H ₄	H	Bn	(93)
3-MeOC ₆ H ₄	H	allyl	(83)
4-MeC ₆ H ₄	H	Bn	(86)
BnCH ₂	H	Bn	(80)
BnCH ₂	Me	Bn	(81)

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

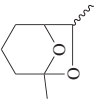
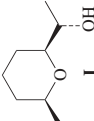
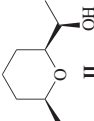
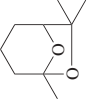
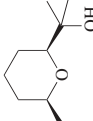
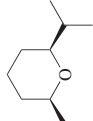
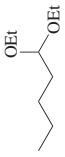

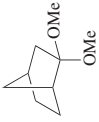
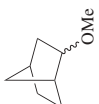
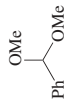

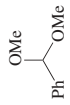
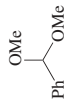
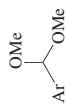

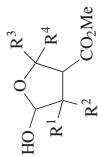
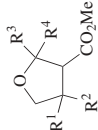
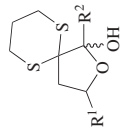
Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₈</div>  endo:exo = 40:60	Et ₃ SiH (10 eq), BF ₃ •OEt ₂ (10 eq), CH ₂ Cl ₂ , 0° to rt, 24 h	 I +  II I + II (85), II = 40:60	485
<div>C₉</div> 	Et ₃ SiH (10 eq), BF ₃ •OEt ₂ (10 eq), CH ₂ Cl ₂ , 0° to rt, 24 h	 (21) +  (45)	485
	Et ₃ SiH (1.2 eq), TFA (30 eq), 50°, 8-10 h	 (75)	327
	Et ₃ SiH (1.1 eq), Nafion [®] -H, CH ₂ Cl ₂ , reflux, 2 h	 (99)	335
	TMSH (1.1 eq), TMSOTf (0.01 eq), CH ₂ Cl ₂ , 0°, 30 min	 I (96)	480
	Et ₃ SiH (1.1 eq), TMSOTf (0.01 eq), CH ₂ Cl ₂ , 0°, 30 min; 29°, 16 h	I (96)	480
	Et ₃ SiH (1.1 eq), Nafion [®] -H, CH ₂ Cl ₂ , reflux, 2 h	I (96)	335

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.																																													
<div>C_{9,13}</div> <div>  </div>	<div> <p>Et₃SiH (1.56 eq), SnX₂ (0.056 mol%), AcBr (2.2 eq), CH₂Cl₂</p> <table> <tr> <th>X</th> <th>Temp</th> <th>Time</th> </tr> <tr> <td>Cl</td> <td>rt</td> <td>3 h</td> </tr> <tr> <td>Br</td> <td>rt</td> <td>3 h</td> </tr> <tr> <td>Cl</td> <td>rt</td> <td>3 h</td> </tr> <tr> <td>Br</td> <td>rt</td> <td>2 h</td> </tr> <tr> <td>Cl</td> <td>rt</td> <td>3 h</td> </tr> <tr> <td>Br</td> <td>rt</td> <td>3 h</td> </tr> <tr> <td>Cl</td> <td>rt</td> <td>12 h</td> </tr> <tr> <td>Br</td> <td>rt</td> <td>2 h</td> </tr> <tr> <td>Cl</td> <td>rt</td> <td>5 h</td> </tr> <tr> <td>Br</td> <td>rt</td> <td>7 h</td> </tr> <tr> <td>Cl</td> <td>0</td> <td>2 h</td> </tr> <tr> <td>Br</td> <td>0</td> <td>1 h</td> </tr> <tr> <td>Cl</td> <td>0</td> <td>5 h</td> </tr> <tr> <td>Br</td> <td>0</td> <td>3 h</td> </tr> </table> </div>	X	Temp	Time	Cl	rt	3 h	Br	rt	3 h	Cl	rt	3 h	Br	rt	2 h	Cl	rt	3 h	Br	rt	3 h	Cl	rt	12 h	Br	rt	2 h	Cl	rt	5 h	Br	rt	7 h	Cl	0	2 h	Br	0	1 h	Cl	0	5 h	Br	0	3 h	<div>  </div>	506
X	Temp	Time																																														
Cl	rt	3 h																																														
Br	rt	3 h																																														
Cl	rt	3 h																																														
Br	rt	2 h																																														
Cl	rt	3 h																																														
Br	rt	3 h																																														
Cl	rt	12 h																																														
Br	rt	2 h																																														
Cl	rt	5 h																																														
Br	rt	7 h																																														
Cl	0	2 h																																														
Br	0	1 h																																														
Cl	0	5 h																																														
Br	0	3 h																																														
<div>C_{9,20}</div> <div>  </div>	<div> <p>Et₃SiH, BF₃•OEt₂, CH₂Cl₂, -78° to rt, 4 h</p> </div>	<div>  </div>	512																																													

R ¹	R ²	R ³	R ⁴
Me	Me	H	Me
Me	Me	Me	Me
—(CH ₂) ₅ —	H	H	Me
Me	Me	H	Ph
—(CH ₂) ₅ —	—(CH ₂) ₅ —		
Me	Me	Ph	Ph

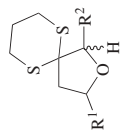
C₉₋₁₆



Ph₃SiH (1 eq), TiCl₄ (1.2 eq),
CH₂Cl₂, -78°, 5 min

R ¹	R ²
Me	Me
Me	Et
Me	Ph
Ph	Me
Et	Ph
<i>i</i> -Pr	Ph







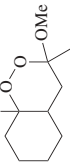
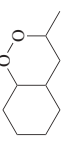
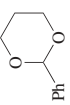

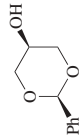

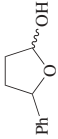
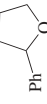
(61)
(43)
(51)
(79)
(48)
(40)



trans:cis
10:1 (70)
7:1 (63)
13:1 (83)
63:1 (72)
16:1 (81)
9:1 (82)

520

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (1.2 eq), TFA (30 eq), 50°, 8-10 h	 (89)	327
	Et_3SiH (2 eq), AlCl_3 (1 eq), HCl, 20°, 1 h	I (93)	146
	Et_3SiH (2 eq), AlCl_3 (1 eq), CH_2Cl_2 , rt, 1 h	I (93)	136
	Et_3SiH (2 eq), AlCl_3 (1 eq), HCl, CH_2Cl_2 , rt, 1 h	I (50)	136
	I_2SiH_2 (1.2 eq), CH_2Cl_2 , rt, 4 h	 (94)	505
	I_2SiH_2 (1.2 eq), CH_2Cl_2 , rt, 4 h	 (81)	505
	Et_3SiH , HOTf	 (39) ^b	499
	PhSiH_3 (3 eq), (Ph_3P) $_3\text{RhCl}$ (0.025 mol%), THF, rt, 48 h	 (91)	493
	PhSiH_3 (4 eq), (Ph_3P) $_3\text{RhCl}$ (0.025 mol%), THF, 60°, 48 h	 (86)	493
	Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$, -45°, 5 min	 (75)	510



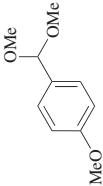
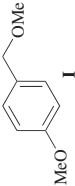
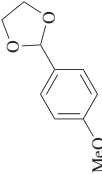
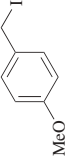
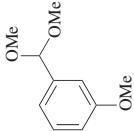
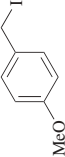
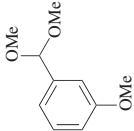
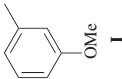
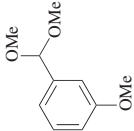
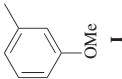

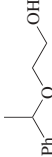
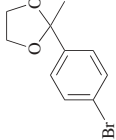
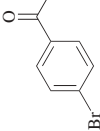
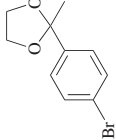
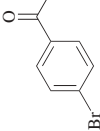
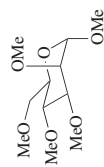
	<p>PhSiH₃ (3 eq), (Ph₃P)₃RhCl (0.025 mol%), THF, 60°, 72 h</p>		(66)	493
	<p>Et₃SiH (4 eq), TCNE (0.3 eq), MeCN, reflux</p>		(85)	500
	<p>PhSiH₃ (3 eq), (Ph₃P)₃RhCl (0.025 mol%), THF, 60°, 48 h</p>		I (77)	493
	<p>I₂SiH₂ (2 eq), CHCl₃, 0°, <2 min</p>		(100)	358
	<p>1. Et₃SiH, SnBr₂-AcBr, CH₂Cl₂, rt, 2.5 h 2. (<i>n</i>-Bu)₃SnH, AIBN, C₆H₆, reflux, 0.5 h</p>		(90)	479
	<p>1. Et₃SiH, SnBr₂-AcBr, CH₂Cl₂, rt, 2.5 h 2. LiAlH₄, THF, rt, 2.5 h</p>		I (92)	479
	<p>PhSiH₃ (3 eq), (Ph₃P)₃RhCl (0.025 mol%), THF, rt, 48 h</p>		(81)	493
	<p>I₂SiH₂ (1 eq), CHCl₃, 0°, 60 min</p>		(35)	358
	<p>I₂SiH₂ (2 eq), CHCl₃, 22°, 2 min</p>		I (100)	358

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

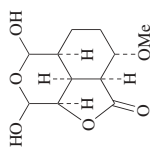
Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₀</p>	Et ₃ SiH (1.1 eq), Nafion [®] -H, CH ₂ Cl ₂ , reflux, 2 h	<p>(91.2)</p>	335
<p>C₁₀₋₁₅</p>	Et ₃ SiH (4 eq), TiCl ₄ (1.2 eq), CH ₂ Cl ₂ , -78°, 3 min	<p>I + II</p> <p>(59) 99:1 (92) 99:1 (100) >99:1</p>	489
<p>C₁₀₋₃₅</p>	Et ₃ SiH (30 eq), BF ₃ •OEt ₂ (30 eq), TFA (12 eq), 0° to rt, 16 h		483
<p>C₁₁</p>	Et ₃ SiH (10 eq), BF ₃ •OEt ₂ (10 eq), CH ₂ Cl ₂ , 0° to rt, 24 h	<p>(70) + (13)</p>	485



Et₃SiH (30 eq), BF₃•OEt₂ (30 eq),
TFA (12 eq), 0° to rt, 16 h

(100)

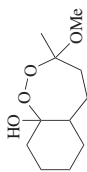
483



Et₃SiH, TFA, 70°, 8 h

(65)

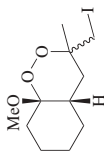
515



Et₃SiH, HOTf

(82)

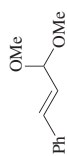
499



Et₃SiH, HOTf

(59)

499

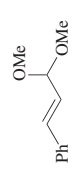

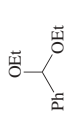

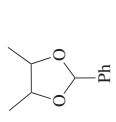
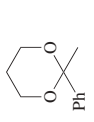

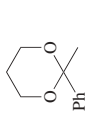
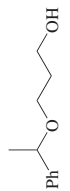
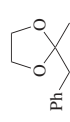
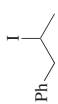
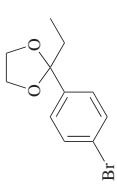
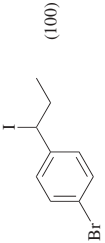
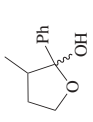

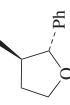


Et₃SiH (4 eq), TCNE (0.3 eq),
MeCN, reflux

(70)

500

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 	1. Et ₃ SiH, SnBr ₂ -AcBr, CH ₂ Cl ₂ , 0°, 5 h 2. LiAlH ₄ , THF, rt, 3.5 h	 (92)	479
	Et ₃ SiH (1.2 eq), TFA (30 eq), 50°, 8–10 h	 (98)	327
	Et ₃ SiH (1.1 eq), Nafion®-H, CH ₂ Cl ₂ , reflux, 1 h	I (97)	335
	I ₂ SiH ₂ (2 eq), CHCl ₃ , 0°, <2 min	 (100)	358
	PhSiH ₃ (3 eq), (Ph ₃ P) ₃ RhCl (0.025 mol%), THF, rt, 48 h	 (89)	493
	I ₂ SiH ₂ (3 eq), CHCl ₃ , 22°, 2 h	 (90)	358
	I ₂ SiH ₂ (2 eq), CHCl ₃ , 0°, <2 min	 (100)	358
	Et ₃ SiH (3 eq), TFA (3 eq), CH ₂ Cl ₂ , -78° to 0°	 I +  II I + II (74), I:II = 1:1	162, 514

C₁₁₋₁₆

<div> <div> <div>TMSO</div> <div>SR³</div> </div> <div> <div>R¹</div> <div>R²</div> </div> <div>R³</div> </div>			
R ¹	R ²	R ³	
—(CH ₂) ₅ —	Et	Et	(96)
Ph	H	Et	(83)
Ph	H	<i>i</i> -Pr	(88)
BnCH ₂	H	Et	(68)
Ph	Me	Et	(97)
<i>n</i> -C ₈ H ₁₇	H	Et	(70)
Ph	H	Ph	(77)

C₁₁₋₁₈

<div> <div> <div>R¹</div> <div>R²</div> <div>OH</div> </div> <div> <div>R¹</div> <div>R²</div> </div> <div>R³</div> </div>			
R ¹	R ²	R ³	
H	Me	Me	(88)
OH	Me	Me	(93)
H	Me	<i>i</i> -Pr	(70)
H	Ph	Me	(86)
H	Ph	<i>i</i> -Pr	(75)

C₁₂



Et₃SiH (1.1 eq), Nafion[®]-H,
CH₂Cl₂, reflux, 2 h

(95)

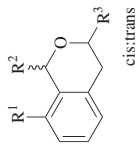
335

Et₃SiH (1.2 eq), TMSCl (50 mol%),
InCl₃ (20 mol%), CH₂Cl₂, rt, 5 h



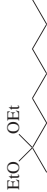
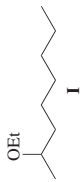
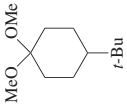
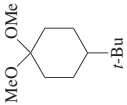
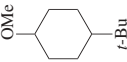
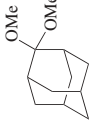
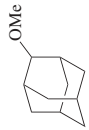
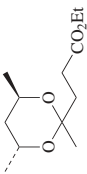
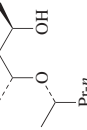
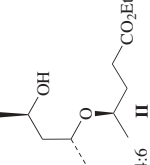
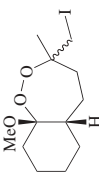
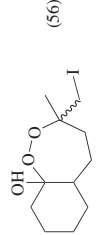


426, 502

Et₃SiH (6 eq), TFA (6 eq),
CH₂Cl₂, -78° to rt, 3 h



514

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂ 	Et ₃ SiH (2 eq), AlCl ₃ (1 eq), HCl, 20°, 1 h	 I (95)	146
	Et ₃ SiH (2 eq), AlCl ₃ (1 eq), HCl, CH ₂ Cl ₂ , rt, 1 h	I (96)	136
	TMSH (1.1 eq), TMSOTf (3.4 mol%), CH ₂ Cl ₂ , 0°, 30 min	 (89) cis:trans = 44:56	480
	Et ₃ SiH (1.1 eq), Nafion [®] -H, CH ₂ Cl ₂ , reflux, 2 h	 (94)	335
	Et ₃ SiH (1.2 eq), TiCl ₄ (1.0 eq), CH ₂ Cl ₂ , -78°	 I +  II (85), I:II = 94:6	491
	Et ₃ SiH, HOTf	 (56)	499
	Et ₃ SiH (1.1 eq), Nafion [®] -H, CH ₂ Cl ₂ , reflux, 2 h	 (97)	335





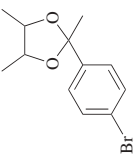

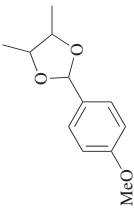

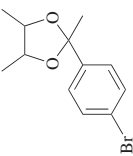
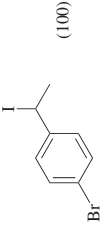
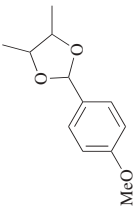
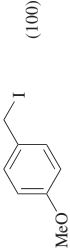
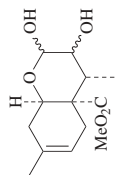
	1. Et ₃ SiH, SnBr ₂ -AcBr, CH ₂ Cl ₂ , 0°, 2 h 2. (<i>n</i> -Bu) ₃ SnH, AIBN, C ₆ H ₆ , reflux, 0.5 h		479
	1. Et ₃ SiH, SnBr ₂ -AcBr, CH ₂ Cl ₂ , 0°, 2.5 h 2. LiAlH ₄ , THF, rt, 15 h	I (82)	479
	1. Et ₃ SiH, SnBr ₂ -AcBr, CH ₂ Cl ₂ , rt, 2 h 2. (<i>n</i> -Bu) ₃ SnH, AIBN, C ₆ H ₆ , reflux, 0.5 h	I (77)	479
	1. Et ₃ SiH, SnBr ₂ -AcBr, CH ₂ Cl ₂ , rt, 4 h 2. (<i>n</i> -Bu) ₃ SnH, AIBN, C ₆ H ₆ , reflux, 0.5 h	I (60) +  (25)	479
	Et ₃ SiH (1.56 eq), SnBr ₂ (0.056 mol%), AcBr (2.2 eq), CH ₂ Cl ₂ , rt, 3 h	 (71)	506
	I ₂ SiH ₂ (2 eq), CHCl ₃ , 0°, 9 min	 (100)	358
	I ₂ SiH ₂ (2 eq), CHCl ₃ , 0°, <2 min	 (100)	358

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

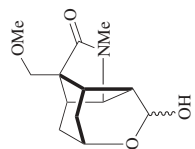
Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.																				
C ₁₂ 	1. Et ₃ SiH, SnBr ₂ ·AcBr, CH ₂ Cl ₂ , rt, 2 h 2. (<i>n</i> -Bu) ₃ SnH, AIBN, C ₆ H ₆ , reflux, 0.5 h	 (77)	479																				
	Et ₃ SiH (3 eq), TFA (3 eq), CH ₂ Cl ₂ , -78° to 0°	 I + II = 1:100	162,514																				
	TMSH (1.1 eq), TMSI (1 mol%), TMSOTf (1.6 mol%), CH ₂ Cl ₂ , 0°, 1 h, rt, 8 h	 (100)	392																				
C ₁₃ 	Et ₃ SiH (x eq), acid (y eq), CH ₂ Cl ₂ , -78°	 I + II = 1:100	491																				
<table border="1"> <thead> <tr> <th>Acid</th><th>x</th><th>y</th><th>Time</th></tr> </thead> <tbody> <tr> <td>TiCl₄</td><td>1.2</td><td>1.2</td><td>0.5 h</td></tr> <tr> <td>SnCl₄</td><td>1.0</td><td>1.0</td><td>0.5 h</td></tr> <tr> <td>AlCl₃</td><td>1.2</td><td>1.2</td><td>8 h</td></tr> <tr> <td>BF₃·OEt₂</td><td>1.0</td><td>1.0</td><td>5 h</td></tr> </tbody> </table>				Acid	x	y	Time	TiCl ₄	1.2	1.2	0.5 h	SnCl ₄	1.0	1.0	0.5 h	AlCl ₃	1.2	1.2	8 h	BF ₃ ·OEt ₂	1.0	1.0	5 h
Acid	x	y	Time																				
TiCl ₄	1.2	1.2	0.5 h																				
SnCl ₄	1.0	1.0	0.5 h																				
AlCl ₃	1.2	1.2	8 h																				
BF ₃ ·OEt ₂	1.0	1.0	5 h																				
	Et ₃ SiH (4 eq), TiCl ₄ (1.2 eq), CH ₂ Cl ₂ , -78°, 0.5 h	 (78) + (13)	488																				



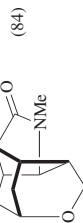
Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$, -78° to -45° , 1 h



510



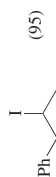
Et_3SiH , TFA, CH_2Cl_2



516



I_2SiH_2 (2 eq), CHCl_3 , 22° , 2 h



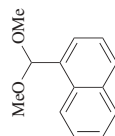
358



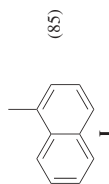
I_2SiH_2 (2 eq), CHCl_3 , 0° , <2 min



358



1. Et_3SiH , $\text{SnBr}_2 \cdot \text{AcBr}$, CH_2Cl_2 , 0° , 1.5 h
2. $(n\text{-Bu})_3\text{SnH}$, AIBN, C_6H_6 , reflux, 0.5 h



479

1. Et_3SiH , $\text{SnBr}_2 \cdot \text{AcBr}$, CH_2Cl_2 , 0° , 1 h
2. LiAlH_4 , THF, rt, 2.5 h

I (84)

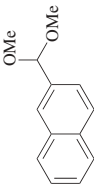
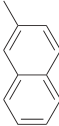
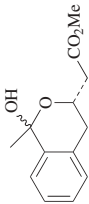
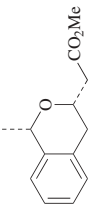
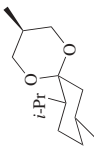
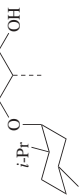
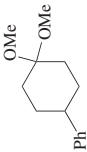

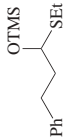

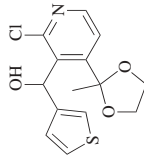
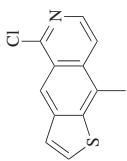
479

1. Et_3SiH , $\text{SnBr}_2 \cdot \text{AcBr}$, CH_2Cl_2 , rt, 4 h
2. $(n\text{-Bu})_3\text{SnH}$, AIBN, C_6H_6 , reflux, 0.75 h

I (72)

479

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃ 	1. Et ₃ SiH, SnBr ₂ -AcBr, CH ₂ Cl ₂ , 0°, 3.5 h 2. (<i>n</i> -Bu) ₃ SnH, AIBN, C ₆ H ₆ , reflux, 0.75 h	 (85)	479
		I (86)	479
	1. Et ₃ SiH, SnBr ₂ -AcBr, CH ₂ Cl ₂ , 0°, 3.5 h 2. LiAlH ₄ , THF, rt, 2.5 h	 (95)	514
C ₁₄ 	Et ₃ SiH (6 eq), TFA (6 eq), CH ₂ Cl ₂ , -78° to rt, 3 h	 (94)	490
	Et ₃ SiH, TiCl ₄ , CH ₂ Cl ₂ , -78°	 (67)	479
	1. Et ₃ SiH, SnBr ₂ -AcBr, CH ₂ Cl ₂ , rt, 24 h 2. (<i>n</i> -Bu) ₃ SnH, AIBN, C ₆ H ₆ , reflux, 0.5 h	 (68)	426, 502
	Et ₃ SiH (1.2 eq), TMSCl (50 mol%), InCl ₃ (20 mol%), CH ₂ Cl ₂ , rt, 5 h	 (60)	486

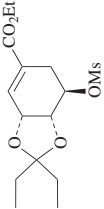
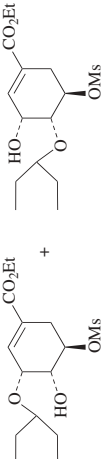
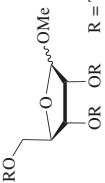
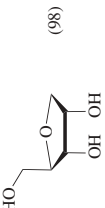
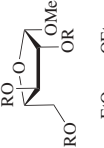
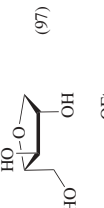
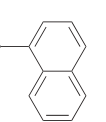
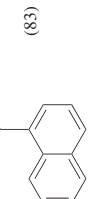
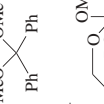
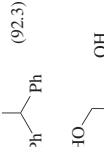
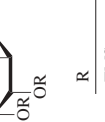
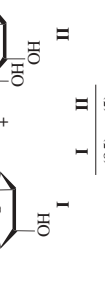
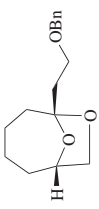
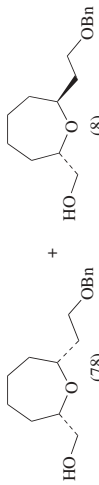
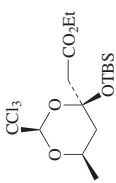
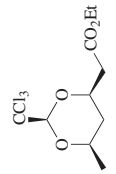
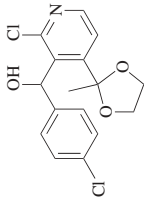
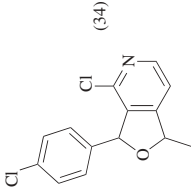
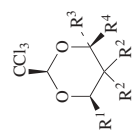
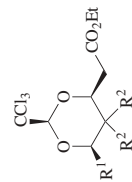
C ₁₅		Et ₃ SiH (1.3 eq), TiCl ₄ (1.1 eq), CH ₂ Cl ₂ , -34°, 2-6 h		498																					
		Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h		503																					
		Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h		503																					
		Et ₃ SiH, FSO ₃ H, TMSNHCNHTMS		487																					
		Et ₃ SiH (1.1 eq), Nafion [®] -H, CH ₂ Cl ₂ , reflux, 3 h		335																					
C ₁₅₋₂₄		Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h		503																					
	<table><tr><th>Catalyst</th><th>I</th><th>II</th></tr><tr><td>TMSOTf</td><td>(95)</td><td>(5)</td></tr><tr><td>TMSOTf</td><td>(35)</td><td>(65)</td></tr><tr><td>TMSOTf</td><td>(25)</td><td>(75)</td></tr><tr><td>TMSOTf</td><td>(17)</td><td>(83)</td></tr><tr><td>Et₃SiOTf</td><td>(77)</td><td>(23)</td></tr><tr><td>Et₃SiOTf</td><td>(26)</td><td>(74)</td></tr></table>	Catalyst	I	II	TMSOTf	(95)	(5)	TMSOTf	(35)	(65)	TMSOTf	(25)	(75)	TMSOTf	(17)	(83)	Et ₃ SiOTf	(77)	(23)	Et ₃ SiOTf	(26)	(74)			
Catalyst	I	II																							
TMSOTf	(95)	(5)																							
TMSOTf	(35)	(65)																							
TMSOTf	(25)	(75)																							
TMSOTf	(17)	(83)																							
Et ₃ SiOTf	(77)	(23)																							
Et ₃ SiOTf	(26)	(74)																							

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₁₆</div> 	Et ₃ SiH (4 eq), TiCl ₄ (1.2 eq), CH ₂ Cl ₂ , -78°, 33 h	 (78)	488
	Et ₃ SiH (1.5 eq), Lewis acid (x eq), CH ₂ Cl ₂ , -23°	 <div> <div>cis:trans</div> <div> <div>(62) 98:2</div> <div>(91) 98:2</div> <div>(54) 97:3</div> <div>(16) 96:4</div> <div>(4) 97:3</div> <div>(1) 91:9</div> </div> </div>	306
	Et ₃ SiH (2 eq), TFA, 0°, 6 h, rt, 15 h	 (34)	486
<div>C₁₆₋₂₅</div> 	Et ₃ SiH (1.5 eq), TiCl ₄ (3.0 eq), CH ₂ Cl ₂ , -23°		306

R ¹	R ²	R ³	R ⁴	cis:trans	
				(92)	>99:1
Me	H	CH ₂ CO ₂ Et	OTBS	(91)	98:2
Me	H	OTBS	CH ₃ CO ₂ Et	(67)	97:3
Ph	H	CH ₃ CO ₂ Et	OTBS	(65)	98:2
Ph	H	OTBS	CH ₂ CO ₂ Et	(97)	>99:1
Ph	Me	OTBS	CH ₂ CO ₂ Et	(94)	>99:1
<i>n</i> -C ₇ H ₁₅	Me	OTBS	CH ₃ CO ₂ Et	(98)	>99:1
BnCH ₂	Me	OTBS	CH ₂ CO ₂ Et		

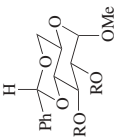
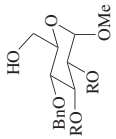
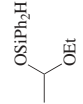

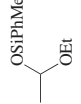



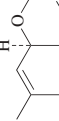

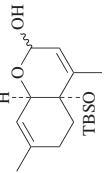
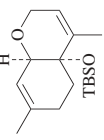
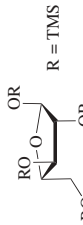
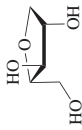
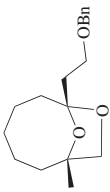
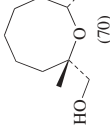
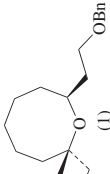
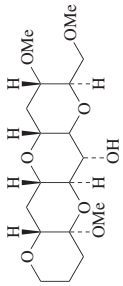
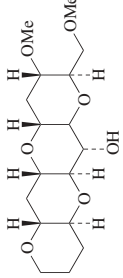
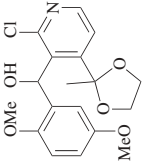
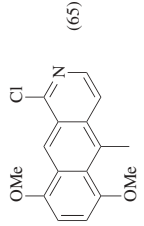
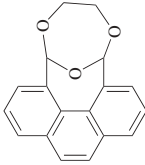
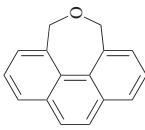
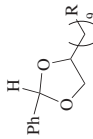
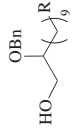
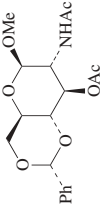
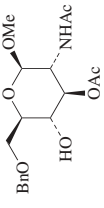
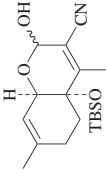
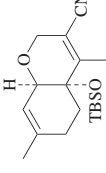
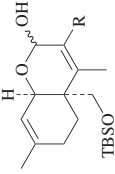
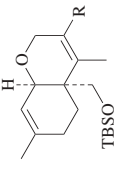
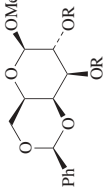
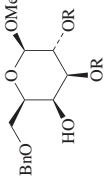
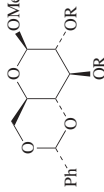
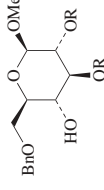
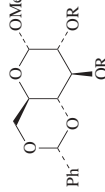
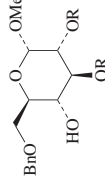
C ₁₆₋₄₆		PMHS, AlCl ₃ (1 eq), Et ₂ O:CH ₂ Cl ₂ (1:1), rt, 12 h		R	
C ₁₆		Ph ₃ Si-O-SiPh ₂ EtO, Ph ₂ SiH ₂ (1.2 eq), Mn(CO) ₅ Ac (1.5-3.0 mol%), C ₆ D ₆ , rt, 4 h		Me (78) Ac (72) Bn (80) TBDPS (65)	496
C ₁₇		Ph ₂ SiH ₂ (1.2 eq), Mn(CO) ₅ Ac (3.0 mol%), C ₆ D ₆ , rt, 2 h		Et-O- (88) + SiHPh ₂ -O-SiHPh ₂ (—)	295
		1. Et ₃ SiH, Sn(OTf) ₂ -AcBr, CH ₂ Cl ₂ , rt, 24 h 2. (<i>n</i> -Bu) ₃ SnH, AIBN, C ₆ H ₆ , reflux, 0.5 h		I (68) + Ph ₂ SiHOEt (—) + PhMe ₂ SiOEt (—) II II:III = 1:1 III	295
		1. <i>i</i> -Bu ₃ AlH, hexanes, MeC ₆ H ₅ , -78°, 2. Et ₃ SiH (1.5 eq), BF ₃ •OEt ₂ (1.1 eq), -78°, 30 min		Ph- (55) + Ph- (9)	479
				(81)	510

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₇</p>  <p>R = TMS</p>	Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h	 <p>(94)</p>	503
<p>C₁₈</p> 	Et ₃ SiH (4 eq), TiCl ₄ (1.2 eq), CH ₂ Cl ₂ , -78°, 15 h	 <p>(70)</p> <p>+</p>  <p>(1)</p>	488
 <p>(82)</p>	Et ₃ SiH, TMSOTf, CH ₂ Cl ₂ , 0°	 <p>(82)</p>	481
 <p>(65)</p>	Et ₃ SiH (1.1 eq), TFA, rt, 18 h	 <p>(65)</p>	486
 <p>(89)</p>	Et ₃ SiH (8 eq), TMSOTf (2 eq), CH ₂ Cl ₂ , -70°, 45 min	 <p>(89)</p>	339
<p>C₁₈₋₂₀</p>  <p>(R)</p>	PMHS, AlCl ₃ (1 eq), Et ₂ O:CH ₂ Cl ₂ (1:1), rt, 12 h	 <p>(69)</p> <p>R</p> <p>N₃ (69)</p> <p>CO₂Me (70)</p>	496

		494
		510
		510
		494
		494
		494

Et₃SiH (5 eq), TFA (5 eq),
CH₂Cl₂, rt, 2-4 h

1. (*i*-Bu)₂AlH, hexanes,
MeC₆H₅, -78°

2. Et₃SiH (1.5 eq), BF₃•OEt₂ (1.1 eq),
-78°, 30 min

Et₃SiH, BF₃•OEt₂, -78°, 30 min

Et₃SiH (5 eq), TFA (5 eq),
CH₂Cl₂, rt, 2-4 h

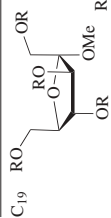
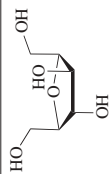
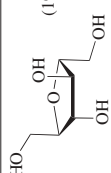
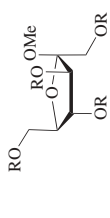
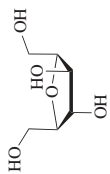
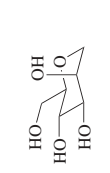
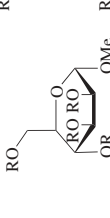
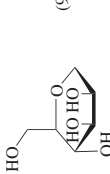
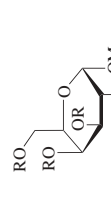
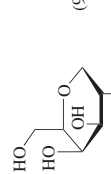
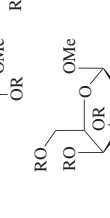
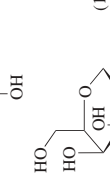
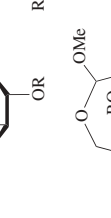
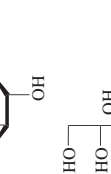
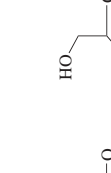
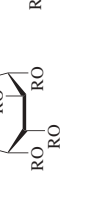
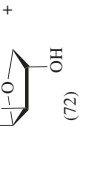
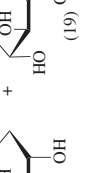
Et₃SiH (5 eq), TFA (5 eq),
CH₂Cl₂, rt, 2-4 h

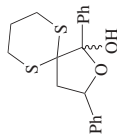
Et₃SiH (5 eq), TFA (5 eq),
CH₂Cl₂, rt, 2-4 h

C₁₈₋₁₉

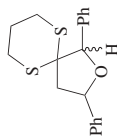
C₁₈₋₂₈

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

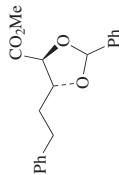
Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₉	Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h	 (78) +  (19)	503
 R = TMS	Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h	 (19) +  (3)	503
 R = TMS	Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h	 (97)	503
 R = TMS	Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h	 (97)	503
 R = TMS	Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h	 (100)	503
 R = TMS	Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h	 (72) +  (9)	503
 R = TMS	Et ₃ SiH (5 eq), TMSOTf (5 eq), MeCN, rt, 16 h	 (9) +  (19)	503



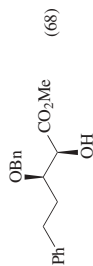
R_3SiH (1 eq), Lewis acid (1.2 eq),
 CH_2Cl_2 , -78° , 5 min



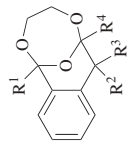
R_3Si	Lewis acid	trans:cis
Ph_3Si	$TiCl_4$	(76) 15:1
Ph_3Si	$TiCl_4$	(87) 16:1
Ph_3Si	$TiCl_4$	(88) 82:1
Ph_3Si	$BF_3 \cdot OEt_2$	(86) 10:1
Ph_3Si	Et_2AlCl	(82) 28:1
Ph_3Si	$EtAlCl_2$	(73) 18:1
Ph_3Si	$AlCl_3$	(76) 11:1
Ph_3Si	$TMSOTf$	(88) 17:1
Ph_2MeSi	$TiCl_4$	(70) 34:1
$PhMe_2Si$	$TiCl_4$	(79) 30:1
Et_3Si	$TiCl_4$	(75) 7:1



$PMHS$, $AlCl_3$ (1 eq),
 $Et_2O:CH_2Cl_2$ (1:1), rt, 12 h

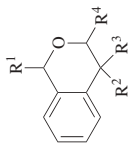


$C_{19,21}$



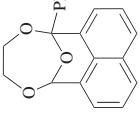
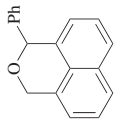
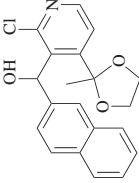
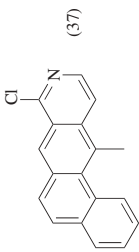
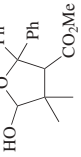
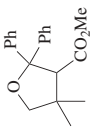
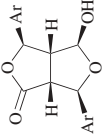
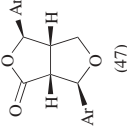


R^1	R^2	R^3	R^4
Ph	Me	Me	H
H	$-(CH_2)_4-$	Ph	Ph
H	Ph	H	Ph

Et_3SiH (8 eq), $TMSOTf$ (2 eq),
 CH_2Cl_2 , -70° , 45 min



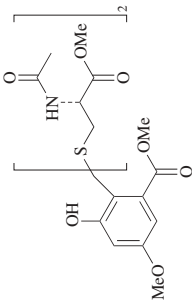
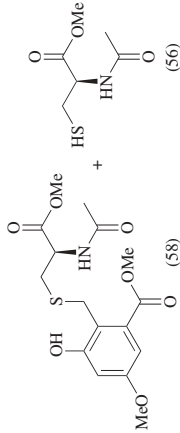
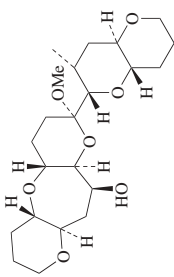
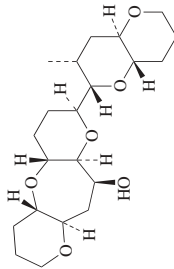
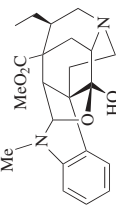
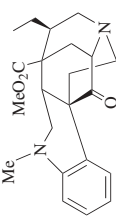
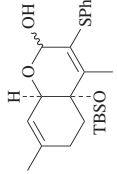
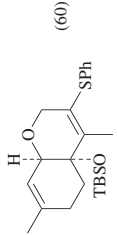
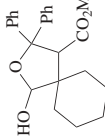
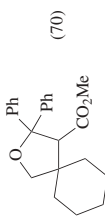
(57)
 (42)
 (53)

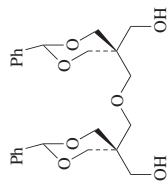
TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
		339	
		468	
		765	
		766	
		766	

C₂₀

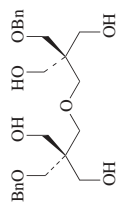
TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₂</p> 	Et ₃ SiH (2.5 eq), TFA, 0°, 2 h	 <p>(58)</p>	768
	Et ₃ SiH, BF ₃ •OEt ₂ , CH ₂ Cl ₂ , MeCN, 0°	 <p>(83)</p>	769
	Et ₃ SiH, TFA	 <p>(—)</p>	770
<p>C₂₃</p> 	1. (<i>i</i> -Bu) ₂ AlH, hexanes, MeC ₆ H ₅ , -78° 2. Et ₃ SiH (1.5 eq), BF ₃ •OEt ₂ (1.1 eq), -78°, 30 min	 <p>(60)</p>	510
	Et ₃ SiH (1.1 eq), BF ₃ •OEt ₂ (1.1 eq), CH ₂ Cl ₂ , -78°, 45 min; rt, 3 h	 <p>(70)</p>	765

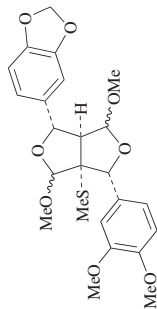
C₂₄

Et₃SiH (13 eq),
BF₃•OEt₂ (12 eq), CH₂Cl₂

(64)

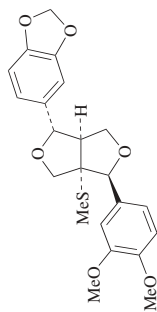


495

C₂₇

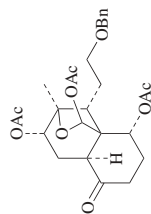
Et₃SiH (4.5 eq),
BF₃•OEt₂ (1.5 eq), CH₂Cl₂,
-78 °C, rt, 48 h

(89)

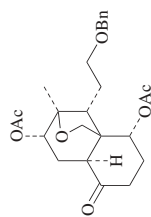


484

Et₃SiH, BF₃•OEt₂, rt, 3 h



(88)



510

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

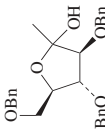
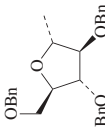
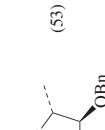
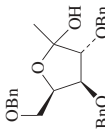
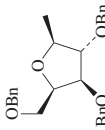
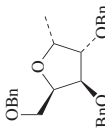
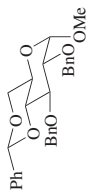
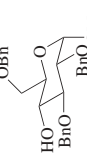

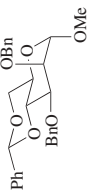
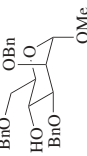

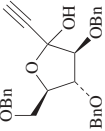
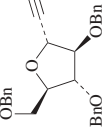
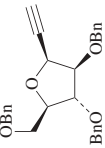
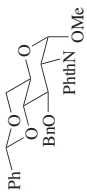
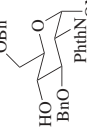

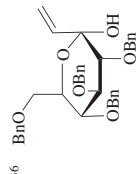
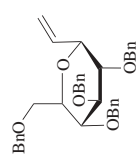
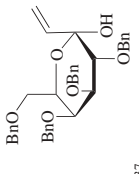
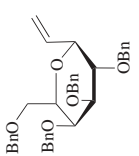
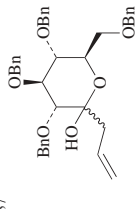
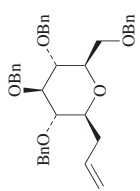
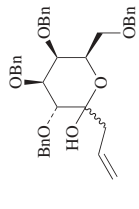
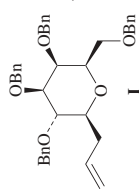
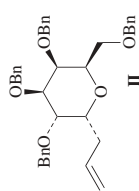
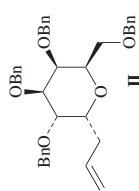
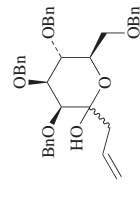
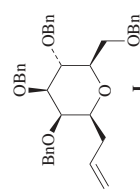
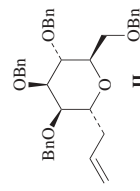
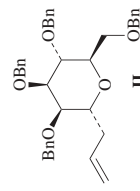
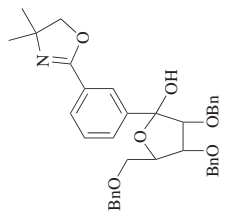
Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
	 Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , -78° 1 h; -10° , 12 h	 (53)	508
	 Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , -78° 1 h; -10° , 12 h	 I + II (76), I:II = 5:1	508
	 Et_3SiH (12 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (2 eq), CH_2Cl_2 , rt, 4 h	 (83)	497
	 Et_3SiH (12 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (2 eq), CH_2Cl_2 , rt, 4 h	 (59)	497
	 Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , -78° 1 h; -10° , 12 h	 I + II (81), I:II = 5:1	508
	 Et_3SiH (12 eq), $\text{BF}_3 \cdot \text{OEt}_2$ (2 eq), CH_2Cl_2 , rt, 4 h	 (85)	497

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

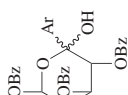
Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₃₆	Et ₃ SiH, TMSOTf	 (35)	519
 C ₃₇	Et ₃ SiH, TMSOTf	 (65)	519
 (85)	Et ₃ SiH, BF ₃ •OEt ₂ , MeCN, 0° to rt	 (85)	507
 I	Et ₃ SiH, BF ₃ •OEt ₂ , MeCN, 0° to rt	 I	507
 II		 II	507
		I + II (76), I:II > 10:1	
 I	Et ₃ SiH, BF ₃ •OEt ₂ , MeCN, 0° to rt	 I	507
 II		 II	507
		I + II (67), I:II = ca. 1:1	



Et₃SiH (2 eq), BF₃•OEt₂ (2 eq),
CH₂Cl₂, -78°, 1 h; 10°, 16 h

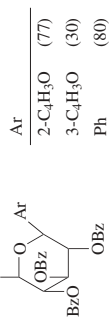
772

C₃₇₋₃₉

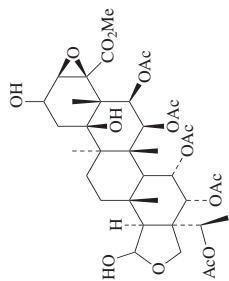


C₃₈

Et₃SiH, BF₃•OEt₂, MeCN, -40° to rt



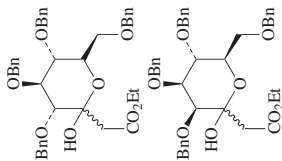
509



Et₃SiH, BF₃•OEt₂, CH₂Cl₂, rt, 1 h

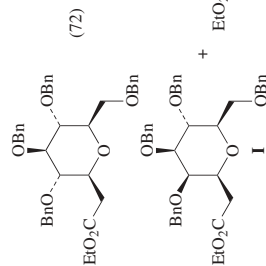
773

(-)



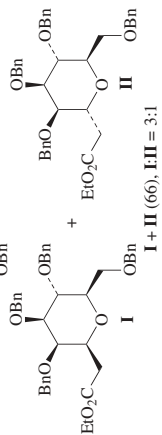
Et₃SiH, BF₃•OEt₂, MeCN, 0° to rt

507



Et₃SiH, BF₃•OEt₂, MeCN, 0° to rt

507

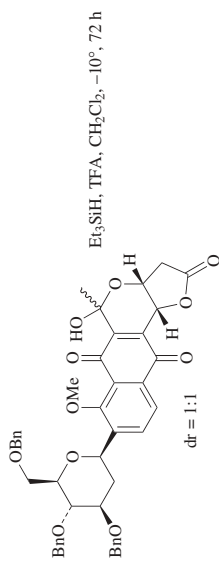


I + II (66), **EH** = 3:1

TABLE 20. ORGANSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

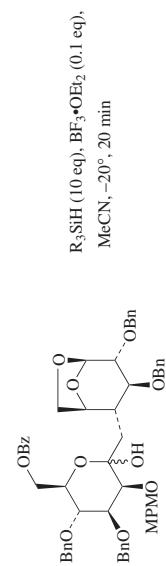
Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₃₉</p>	<p>Et₃SiH (5 eq), TFA (5 eq), (CF₃CO)₂O (3 eq), CH₂Cl₂, rt, 2-4 h</p>	<p>(83)</p>	494
<p>C₄₀</p>	<p>Et₃SiH (5 eq), TFA (5 eq), (CF₃CO)₂O (3 eq), CH₂Cl₂, rt, 2-4 h</p>	<p>(78)</p>	494
<p>C₄₀</p>	Et ₃ SiH, TMSOTf	(—)	519
<p>C₄₂</p>	Et ₃ SiH, TMSOTf	(—)	519
	Et ₃ SiH, TMSOTf CH ₂ Cl ₂ , 0°	(70)	482

C44

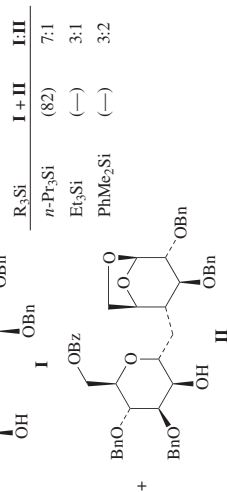


513

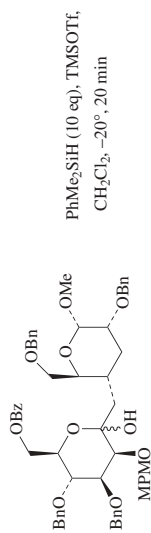
C56



517, 774

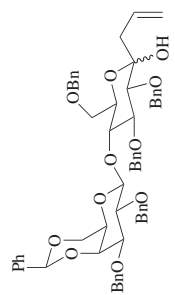
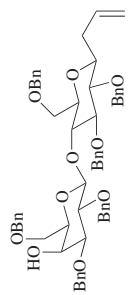


C57



517

TABLE 20. ORGANOSILANE REDUCTION OF ACETALS, KETALS, AND HEMIKETALS (Continued)

Acetal/Ketal	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C57</p> 	<p>Et₃SiH (12 eq), BF₃•OEt₂ (2 eq), CH₂Cl₂, rt, 4 h</p>	 <p>(73)</p>	497

^a The yield was determined by NMR spectroscopy.

^b The product is a single isomer of undetermined configuration.

TABLE 21. ORGANOSILANE REDUCTION OF AMINALS AND HEMIAMINALS

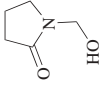

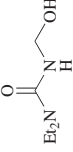
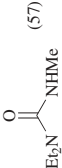
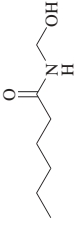
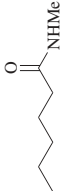
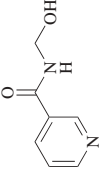
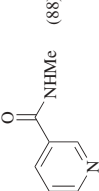
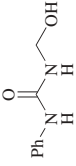
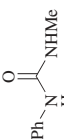
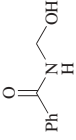

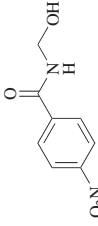
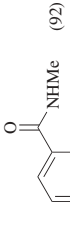
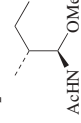
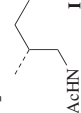


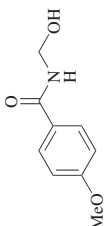
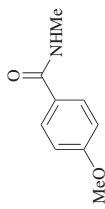
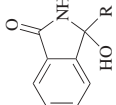
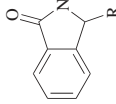
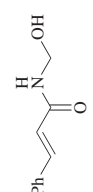
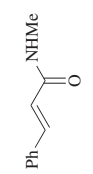
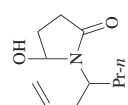
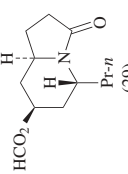
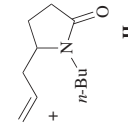

Aminal	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₅	Et ₃ SiH (1.5 eq), TFA (10 eq), CHCl ₃ , rt, 1-4 h	 (84)	526
 C ₆	Et ₃ SiH (1.5 eq), TFA (10 eq), CHCl ₃ , rt, 1-4 h	 (57)	526
 C ₇	Et ₃ SiH (1.5 eq), TFA (10 eq), CHCl ₃ , rt, 1-4 h	 (86)	526
 C ₈	Et ₃ SiH (1.5 eq), TFA (10 eq), CHCl ₃ , reflux, 2 h	 (88)	526
 C ₈	Et ₃ SiH (1.5 eq), TFA (10 eq), CHCl ₃ , rt, 1-4 h	 (85)	526
 C ₈	Et ₃ SiH (1.5 eq), TFA (10 eq), CHCl ₃ , rt, 1-4 h	 (94)	526
 C ₈	Et ₃ SiH (1.5 eq), TFA (10 eq), CHCl ₃ , rt, 1-4 h	 (92)	526
 C ₈	Et ₃ SiH (1.2 eq), BF ₃ •OEt ₂ (1.2 eq), CH ₂ Cl ₂ , 5°, 2 h	 (84)	521
 C ₈	Et ₃ SiH (1.2 eq), TFA (3 eq), CH ₂ Cl ₂ , 5° to rt, 2 h	 (75)	521

TABLE 21. ORGANOSILANE REDUCTION OF AMINALS AND HEMIAMINALS (Continued)

Aminal	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 	Et ₃ SiH (1.5 eq), TFA (10 eq), CHCl ₃ , rt, 1-4 h	 (91)	526
C ₉₋₁₅ 	Et ₃ SiH (10 eq), BF ₃ •OEt ₂ (3 eq), CH ₂ Cl ₂ , -15° to rt, 16 h	 R	527
		(65)	
		(96)	
		(75)	
		(97)	
		(55)	
		(91)	
		(96)	
		(90)	
		(88)	
C ₁₀ 	Et ₃ SiH (1.5 eq), TFA (10 eq), CHCl ₃ , rt, 1-4 h	 (85)	526
C ₁₁ 	Et ₃ SiH, HCO ₂ H, CH ₂ Cl ₂ , rt, 10 h	 (29) +  +  (775) I + II (42), I:II = 3:5	775

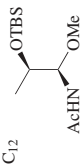
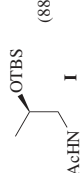
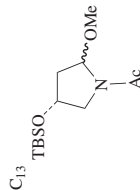
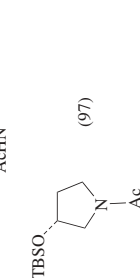
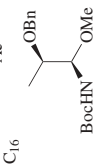
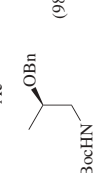
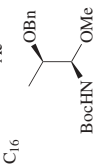
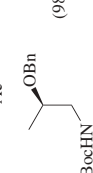
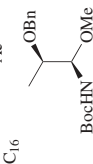
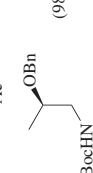
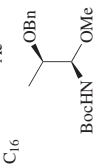
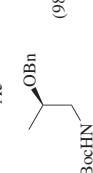
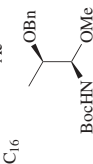
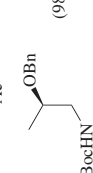
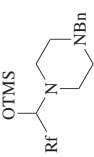
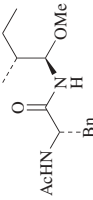
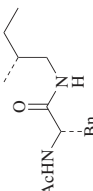
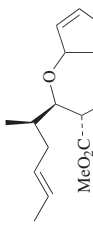
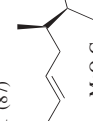
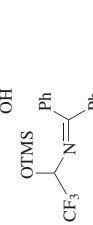
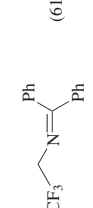
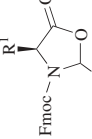
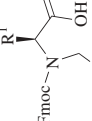


		Et ₃ SiH (2 eq), BF ₃ •OEt ₂ (2 eq), CH ₂ Cl ₂ , -40°, 1-2 h	521
		Et ₃ SiH (1.2 eq), TFA (3 eq), CH ₂ Cl ₂ , 5° to rt, 2 h	521
		Et ₃ SiH (2 eq), BF ₃ •OEt ₂ (2 eq), CH ₂ Cl ₂ , -40°, 1-2 h	521
		Et ₃ SiH (2 eq), BF ₃ •OEt ₂ (2 eq), CH ₂ Cl ₂ , -40°, 1-2 h	521
		Et ₃ SiH, TFA, CH ₂ Cl ₂ , 15 min	524
		1. TFA, CH ₂ Cl ₂ , 30 min 2. Et ₃ SiH, 0°, 30 min	524
		1. TiCl ₄ , CH ₂ Cl ₂ , -78°, 30 min 2. Et ₃ SiH, 0°, 30 min	524

TABLE 21. ORGANOSILANE REDUCTION OF AMINALS AND HEMIAMINALS (Continued)

Aminal	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₆₋₁₇ 	Et ₃ SiH (1 eq), BF ₃ •OEt ₂ (1 eq), CH ₂ Cl ₂ , rt, 5 h	Rf <div>CF₃ (85)</div> <div>CClF₂ (80)</div> <div>CF₃CF₂ (84)</div>	522
C ₁₇ 	Et ₃ SiH (1.2 eq), BF ₃ •OEt ₂ (1.2 eq), CH ₂ Cl ₂ , 5°, 2 h	 (89)	521
C ₁₈ 	Et ₃ SiH (1.2 eq), TFA (3 eq), CH ₂ Cl ₂ , 5° to rt, 2 h	 (87)	521
C ₁₉₋₂₈ 	Et ₃ SiH (3 eq), TFA (xs), CHCl ₃ , rt, 20 h	 (63)	525
C ₁₈ 	Et ₃ SiH (1 eq), BF ₃ •OEt ₂ (1 eq), CH ₂ Cl ₂ , 50°, 24 h	 (61)	522
C ₁₉₋₂₈ 	Et ₃ SiH (3 eq), TFA, CHCl ₃ , rt, 22 h	 (67)	528

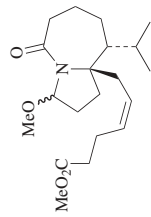
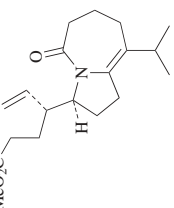
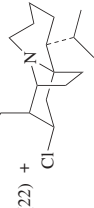
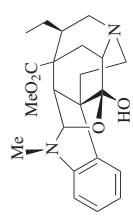
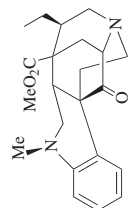
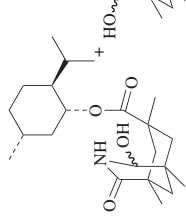
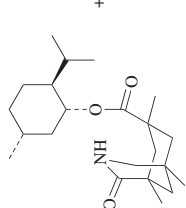

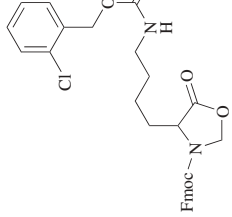
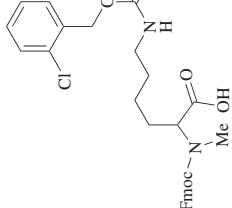
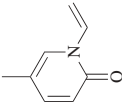
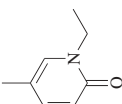
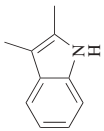
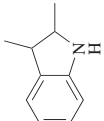
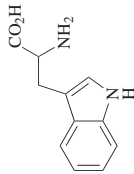
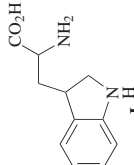
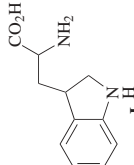
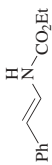

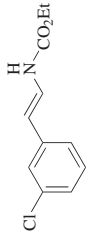
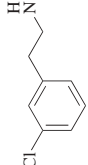
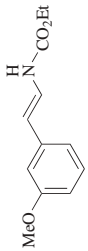
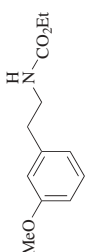
C ₂₀		1. TiCl ₄ , CH ₂ Cl ₂ , -78° to 0° 2. Et ₃ SiH		(22) + 	524
C ₂₂		Et ₃ SiH, TFA		(-)	770
C ₂₃		Et ₃ SiH, TFA			776
C ₃₀		Et ₃ SiH (3 eq), TFA, CHCl ₃ , rt, 22 h		(15)	528

TABLE 22. ORGANOSILANE REDUCTION OF ENAMINES

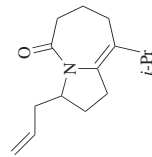
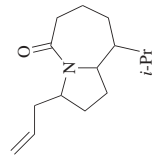
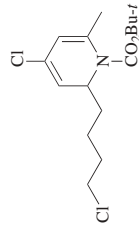
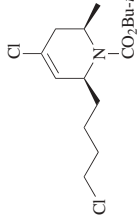
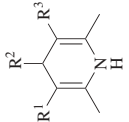
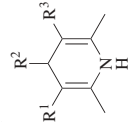
Enamine	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3SiH (5 eq), TFA (10 eq), 65° , 25 h	 (67)	235
	Et_3SiH (1.4 eq), TFA, 60° , 48 h	 (80) cis:trans = 42:58	533
	Et_3SiH (5 eq), TFA, CH_2Cl_2 , rt, 2 h	 I (4%) ^a	532
	$(i\text{-Pr})_3\text{SiH}$ (5 eq), TFA, CH_2Cl_2 , rt, 2 h	 I (4%) ^a	532
	Et_3SiH (1.5 eq), TFA, -10° , 0.5 h	 (92)	535
	Et_3SiH (1.5 eq), TFA, -10° , 0.5 h	 (94)	535
	Et_3SiH (1.5 eq), TFA, -10° , 0.5 h	 (99)	535

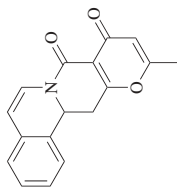
C ₁₂		Et ₃ SiH (1.5 eq), TFA, -10°, 0.5 h		535
C ₁₃		Et ₃ SiD (1.5 eq), TFA-d ₁ , -10°, 0.5 h		535
C ₁₄		Et ₃ SiH (1.5 eq), TFA, -10°, 0.5 h		535
C ₁₄₊₂₁		Et ₃ SiH (1.05 eq), TFA (1 eq), CH ₂ Cl ₂ , 0°, 6 h; rt, 6 h		536
		Et ₃ SiH (3 eq), TFA, CH ₂ Cl ₂ , rt		538

Time	
9 h	(95)
6.5 h	(80)
5 h	(80)
20 h	(33)

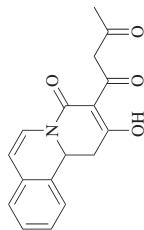
R ¹	R ²	R ³	R ⁴
OMe	H	H	H
OMe	OMe	H	H
OMe	H	H	OMe
H	OBn	OMe	H

TABLE 22. ORGANOSILANE REDUCTION OF ENAMINES (Continued)

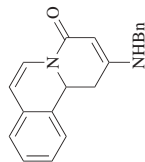
Enamine	Conditions	Product(s) and Yield(s) (%)	Refs.																												
 C ₁₅	Et ₃ SiH, TFA, CH ₂ Cl ₂ , 15 min	 (74) dr = 1:1	524																												
 C ₁₆₋₁₇	Et ₃ SiH, TFA, CH ₂ Cl ₂ , -42°	 (70)	777																												
 C ₁₆₋₁₉	Et ₃ SiH (1 eq), TFA, 20°	<table border="1"> <thead> <tr> <th>R¹</th><th>R²</th><th>R³</th><th></th></tr> </thead> <tbody> <tr> <td>CO₂Me</td><td>3-O₂NC₆H₄</td><td>CN</td><td>(63)</td></tr> <tr> <td>CO₂Me</td><td>Ph</td><td>CO₂Me</td><td>(58)</td></tr> <tr> <td>CO₂Me</td><td>2-O₂NC₆H₄</td><td>CO₂Me</td><td>(66)</td></tr> <tr> <td>CO₂Me</td><td>2-CF₃C₆H₄</td><td>CO₂Me</td><td>(69)</td></tr> <tr> <td>Ac</td><td>3-O₂NC₆H₄</td><td>Ac</td><td>(64)</td></tr> </tbody> </table>	R ¹	R ²	R ³		CO ₂ Me	3-O ₂ NC ₆ H ₄	CN	(63)	CO ₂ Me	Ph	CO ₂ Me	(58)	CO ₂ Me	2-O ₂ NC ₆ H ₄	CO ₂ Me	(66)	CO ₂ Me	2-CF ₃ C ₆ H ₄	CO ₂ Me	(69)	Ac	3-O ₂ NC ₆ H ₄	Ac	(64)	529				
R ¹	R ²	R ³																													
CO ₂ Me	3-O ₂ NC ₆ H ₄	CN	(63)																												
CO ₂ Me	Ph	CO ₂ Me	(58)																												
CO ₂ Me	2-O ₂ NC ₆ H ₄	CO ₂ Me	(66)																												
CO ₂ Me	2-CF ₃ C ₆ H ₄	CO ₂ Me	(69)																												
Ac	3-O ₂ NC ₆ H ₄	Ac	(64)																												
 C ₁₆₋₁₉	Et ₃ SiH (3 eq), TFA, 50°	<table border="1"> <thead> <tr> <th>R¹</th><th>R²</th><th>R³</th><th></th></tr> </thead> <tbody> <tr> <td>CO₂Me</td><td>3-O₂NC₆H₄</td><td>CN</td><td>(89)</td></tr> <tr> <td>CO₂Me</td><td>Ph</td><td>CO₂Me</td><td>(55)</td></tr> <tr> <td>CO₂Me</td><td>2-O₂NC₆H₄</td><td>CO₂Me</td><td>(94)</td></tr> <tr> <td>CO₂Me</td><td>2-CF₃C₆H₄</td><td>CO₂Me</td><td>(56)</td></tr> <tr> <td>Ac</td><td>3-O₂NC₆H₄</td><td>Ac</td><td>(60)</td></tr> <tr> <td>EtO₂C</td><td>3-O₂NC₆H₄</td><td>EtO₂C</td><td>(72)</td></tr> </tbody> </table>	R ¹	R ²	R ³		CO ₂ Me	3-O ₂ NC ₆ H ₄	CN	(89)	CO ₂ Me	Ph	CO ₂ Me	(55)	CO ₂ Me	2-O ₂ NC ₆ H ₄	CO ₂ Me	(94)	CO ₂ Me	2-CF ₃ C ₆ H ₄	CO ₂ Me	(56)	Ac	3-O ₂ NC ₆ H ₄	Ac	(60)	EtO ₂ C	3-O ₂ NC ₆ H ₄	EtO ₂ C	(72)	529
R ¹	R ²	R ³																													
CO ₂ Me	3-O ₂ NC ₆ H ₄	CN	(89)																												
CO ₂ Me	Ph	CO ₂ Me	(55)																												
CO ₂ Me	2-O ₂ NC ₆ H ₄	CO ₂ Me	(94)																												
CO ₂ Me	2-CF ₃ C ₆ H ₄	CO ₂ Me	(56)																												
Ac	3-O ₂ NC ₆ H ₄	Ac	(60)																												
EtO ₂ C	3-O ₂ NC ₆ H ₄	EtO ₂ C	(72)																												

C₁₇Et₃SiH (9 eq), TFA, CHCl₃, 20°, 24 h

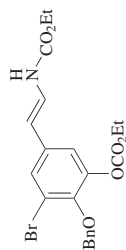
537

C₁₈Et₃SiH, TFA, CHCl₃, 20°, 24 h

537

C₂₀Et₃SiH, TFA, CHCl₃, 20°, 24 h

537

C₂₁Et₃SiH¹ (1.5 eq), acid, -10°, 0.5 h

535

R ¹	Acid	
	D	TFA
H	H	TFA-d ₁
H	H	TFA

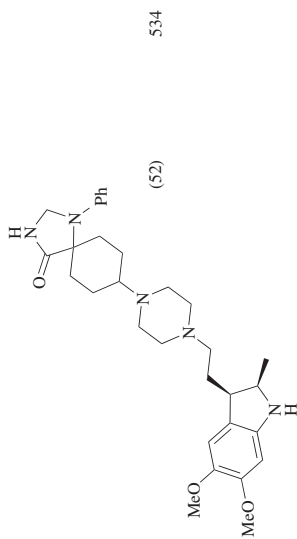
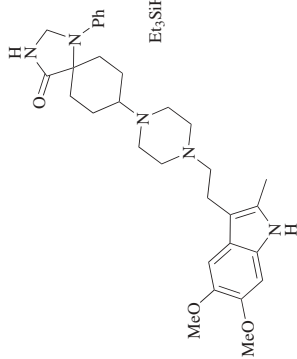
R ²	R ³		
		H	D (63)
Br	BnO	D	H (77)
R ²	R ³	H	H (94)

TABLE 22. ORGANOSILANE REDUCTION OF ENAMINES (Continued)

Enamine	Conditions	Product(s) and Yield(s) (%)	Refs.															
C ₂₁₋₂₃ 	Et ₃ SiH (2 eq), TFA, 50°, 64 h	<table><tr><th>R¹</th><th>R²</th><th>Yield (%)</th></tr><tr><td>Br</td><td>H</td><td>(25)</td></tr><tr><td>F</td><td>H</td><td>(32)</td></tr><tr><td>Cl</td><td>Cl</td><td>(14)</td></tr><tr><td>OMe</td><td>OMe</td><td>(80)</td></tr></table>	R ¹	R ²	Yield (%)	Br	H	(25)	F	H	(32)	Cl	Cl	(14)	OMe	OMe	(80)	534
R ¹	R ²	Yield (%)																
Br	H	(25)																
F	H	(32)																
Cl	Cl	(14)																
OMe	OMe	(80)																
C ₂₂ 	Et ₃ SiH (6 eq), TFA (10 eq), CH ₂ Cl ₂ , -42°, 4 h	<p>I + II + III (79) I:II:III = 75:10:15</p>	531															
C ₂₇ 	(<i>i</i> -Pr) ₃ SiH (6 eq), TFA (10 eq), CH ₂ Cl ₂ , -42°, 4 h	<p>I + II + III (95), I:II:III = 78.9:13</p>	531															
	Et ₃ SiH (2 eq), TFA, rt, 1 h	<p>(81)</p>	530															
	R ₃ SiH (x eq), TFA, 20°	<p>I + II + III</p>	530															


C₃₁

R ₃ Si	x	Time	I + II + III	II:III
Et ₃ Si	2	1.5 h	(—)	19:17:64
Et ₃ Si	2	18 h	(—)	—
Et ₃ Si	2	1 h	(—)	—
PhMe ₂ Si	3	18 h	(—)	46:44:10
Ph ₃ Si	3	18 h	(—)	—

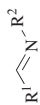


534

^a The yield was determined by NMR spectroscopy.

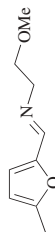
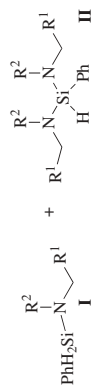
Ar	R ¹	R ²	Temp	Time
Ph	H	Me	70°	48 h
Ph	H	allyl	70°	26 h
Ph	H	<i>i</i> -Bu	rt	0.5 h
Ph	H	Boc	rt	0.5 h
Ph	H	SO ₂ Ph	rt	0.5 h
Ph	H	Ph	rt	1 h
Ph	H	Bn	70°	3 h
Ph	H	4-MeOC ₆ H ₄	70°	1.5 h
Ph	H	2-MeOC ₆ H ₄	rt	2 h
4-MeOC ₆ H ₄	H	Bn	70°	17.5 h
Ph	Me	Bn	rt	4 h
	Bn	Bn	rt	23 h
Ph	Ph	Bn	rt	96 h

C₉



PhSiH₃ (1 eq), catalyst (10 mol%),
THF, rt, 20 h

544

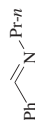


Cl₃SiH (1.2 eq), BF₃•OEt₂,
C₆H₆, reflux, 4 h

545



C₁₀



Cl₃SiH (1.2 eq), BF₃•OEt₂,
C₆H₆, reflux, 4 h

545

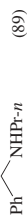


TABLE 23. ORGANOSILANE REDUCTION OF IMINES (Continued)

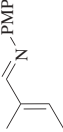
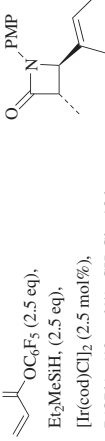
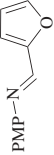
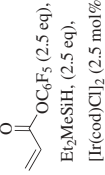
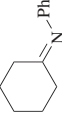
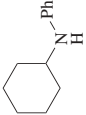



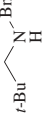

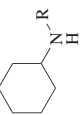
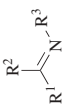

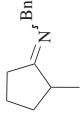
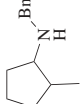
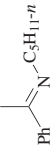
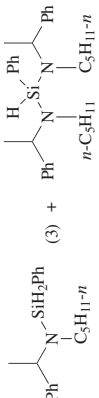
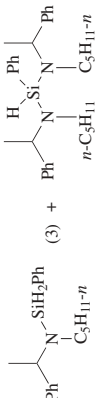
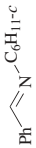
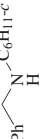
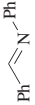
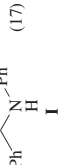
		<p>OC₆F₅ (2.5 eq), Et₂MeSiH, (2.5 eq), [Ir(cod)Cl]₂ (2.5 mol%), P(OPh)₃ (10 mol%), CH₂Cl₂, 18 h</p>	(60) trans:cis > 20:1	476
		<p>OC₆F₅ (2.5 eq), Et₂MeSiH, (2.5 eq), [Ir(cod)Cl]₂ (2.5 mol%), P(OPh)₃ (10 mol%), CH₂Cl₂, 18 h</p>	(78) trans:cis > 20:1	476
		<p>Cl₃SiH (1.2 eq), BF₃•OEt₂, C₆H₆, reflux, 4 h</p>	(81)	545
		<p>PhSiH₃ (1 eq), 230 (10 mol%), THF, rt, 20 h</p>	(52) + $n\text{-C}_3\text{H}_{11}\text{-}n$ (35)	544
		<p>PMHS, EtOH, <i>n</i>-butyltris(EH)ün, rt</p>	(75)	543
		<p>Cl₃SiH, MeCN, reflux, 4 h</p>	(48)	542

TABLE 23. ORGANOSILANE REDUCTION OF IMINES (Continued)

Imine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂₋₁₅ 	PMHS (3 eq), <i>n</i> -BuSn(O ₂ CCH(Et)Bu- <i>n</i>) ₃ (0.1 eq), EtOH, rt		543
	Time		
	20 h	(75)	
	7 h	(82)	
	10 h	(76)	
	6 h	(81)	
C ₁₃ 	PMHS, EtOH, rt, <i>n</i> -butyltris(EH)tin (0.1 eq), rt, 9 h		543
	PhSiH ₃ (1 eq), 230 (10 mol%), THF, rt, 20 h	 (3) +  (17)	544
	Cl ₃ SiH, MeCN, reflux, 4 h	 (60)	542
	Cl ₃ SiH (1.2 eq), C ₆ H ₆ , reflux, 4 h	 (17)	545
	Cl ₃ SiH (1.2 eq), BF ₃ •OEt ₂ , C ₆ H ₆ , reflux, 4 h	I (40)	545
	PMHS, EtOH, rt, <i>n</i> -butyltris(EH)tin	I (82)	543
	Et ₃ SiH (1 eq), TFA (3 eq), 70°, 1.5 h	I (80)	541

208	I (71)	Et_3SiH (1.1–1.2 eq), HCO_2H , HOAc, KU-1, 55°, 5 h
539	I (67)	PMHS (5 eq), ZnCl_2 (2 eq), Et_2O , rt, 10 h
539	I (67)	PMHS (5 eq), ZnCl_2 (2 eq), Et_2O , rt, 10 h
544	(47)	PhSiH_3 (1 eq), 230 (10 mol%), THF, rt, 20 h
476	(20) dr > 20:1	Et_2MeSiH , (1 eq) 230 (2.5 mol%), ligand (x mol%), CH_2Cl_2 , 18 h

230

47

TABLE 23. ORGANOSILANE REDUCTION OF IMINES (Continued)

Imine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃			
	 Et ₃ MeSiH (2.5 eq), [Ir(cod)Cl] ₂ (2.5 mol%), P(OPh) ₃ (10 mol%), CH ₂ Cl ₂ , 18 h	 (68) trans:cis = —	476
	PMHS (5 eq), ZnCl ₂ (2 eq), Et ₂ O, rt, 12 h	 (75)	539
C ₁₃₋₁₄			
	Et ₃ SiH (1 eq), TFA (3 eq), 60-70°, 30-60 min	 R ¹ R ² H H (78) Me H (86) H Me (95)	540
C ₁₃₋₁₅			
	(MeO) ₃ SiH (1.2 eq), LiOMe (4 mol%), THF, rt, 0.5 h	 R ¹ R ² NHTs	294
	Time		
	48 h	(62)	
	67 h	(84)	
	42 h	(100)	
	56 h	(92)	
	50 h	(80)	
	59 h	(63)	
	59 h	(97)	
	50 h	(80)	

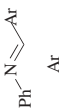

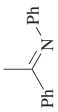
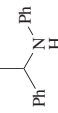
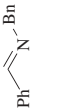
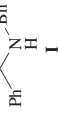

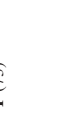

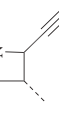

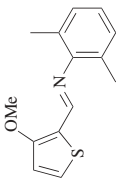
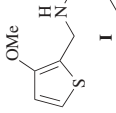



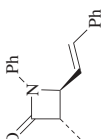

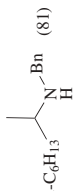
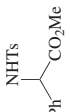
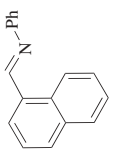
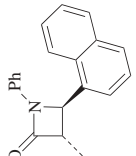
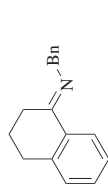
C ₁₃₋₁₆			Cl ₃ SiH, MeCN, reflux, 4 h	542
	Ar			
	Ph			(79)
	4-ClC ₆ H ₄			(69)
	2-ClC ₆ H ₄			(62)
	4-MeOC ₆ H ₄			(78)
	2-MeOC ₆ H ₄			(88)
	3-MeOC ₆ H ₄			(76)
	4-(<i>i</i> -Pr)C ₆ H ₄			(73)
C ₁₄			PMHS (5 eq), ZnCl ₂ (2 eq), Et ₂ O, rt, 15 h	539
			PMHS, <i>n</i> -butyltris(EH)tin, EtOH, rt	543
			PMHS (5 eq), ZnCl ₂ (2 eq), Et ₂ O, rt, 10 h	539
				476
			Cl ₃ SiH (1.2 eq), BF ₃ •OEt ₂ , C ₆ H ₆ , reflux, 4 h	545
			Cl ₂ SiH ₂ (1.2 eq), C ₆ H ₆ , reflux, 4 h	545

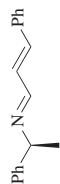
TABLE 23. ORGANOSILANE REDUCTION OF IMINES (Continued)

Imine	Conditions	Product(s) and Yield(s) (%)	Refs.										
C ₁₅	 OC ₆ F ₅ (2.5 eq), Et ₂ MeSiH (2.5 eq), [Ir(cod)Cl] ₂ (2.5 mol%), P(OPh) ₃ (10 mol%), CH ₂ Cl ₂ , 18 h	 (70) trans:cis = 5.2:1	476										
	PMHS (5 eq), ZnCl ₂ (2 eq), Et ₂ O, rt, 20 h	 (55)	539										
C ₁₆	PMHS, <i>n</i> -butyltris(EH)tin, EtOH, rt	 <i>n</i> -C ₆ H ₁₃ (81)	543										
	Ph ₂ SiH ₂ (1.2 eq), catalyst (1 eq), CH ₂ Cl ₂	 NHTs	373										
	<table><tr><th>Catalyst</th><th>Temp</th></tr><tr><td>AlCl₃</td><td>20°</td></tr><tr><td>TiCl₄</td><td>20°</td></tr><tr><td>BF₃•OEt₂</td><td>20°</td></tr><tr><td>ZnCl₂</td><td>40°</td></tr></table>	Catalyst	Temp	AlCl ₃	20°	TiCl ₄	20°	BF ₃ •OEt ₂	20°	ZnCl ₂	40°	(90) (90) (63) (48)	
Catalyst	Temp												
AlCl ₃	20°												
TiCl ₄	20°												
BF ₃ •OEt ₂	20°												
ZnCl ₂	40°												
C ₁₇	 OC ₆ F ₅ (2.5 eq), Et ₂ MeSiH (2.5 eq), [Ir(cod)Cl] ₂ (2.5 mol%), P(OPh) ₃ (10 mol%), CH ₂ Cl ₂ , 18 h	 (80) trans:cis > 20:1	476										



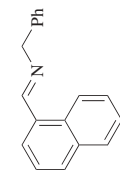
PMHS (3 eq),
n-butyltris(EH)tin (0.1 eq),
 EtOH, rt, 10 h

543



PMHS (5 eq), ZnCl₂ (2 eq),
 Et₂O, rt, 24 h

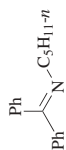
539



C₁₈

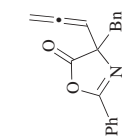
PMHS (5 eq), ZnCl₂ (2 eq),
 Et₂O, rt, 12 h

539



PhSiH₃ (1 eq), **230** (10 mol%),
 THF, rt, 20 h

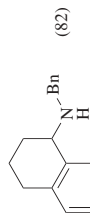
544



C₁₉

Et₃SiH, Cl₃CCO₂H

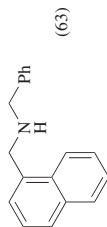
778



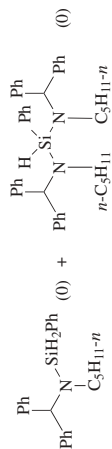
(82)



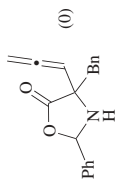
(50)



(63)



(0)



(0)

TABLE 23. ORGANOSILANE REDUCTION OF IMINES (Continued)

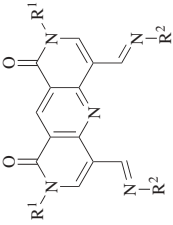
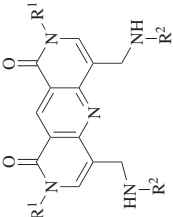
Imine	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p> Et_2SiH_2 (2.2 eq), $(\text{Ph}_3\text{P})_3\text{RhCl}$, CH_2Cl_2, rt, 16 h </p>		547
<p> R^1 R^2 </p> <hr/> <p> $\text{Cl}(\text{CH}_2)_4$ Ph $\text{Cl}(\text{CH}_2)_4$ 3-O₂NC₆H₄ $\text{Cl}(\text{CH}_2)_4$ PhCH(OH)CHMe allyl PhCH(OH)CHMe </p>		<p>(81)</p> <p>(82)</p> <p>(78)</p> <p>(69)</p>	

TABLE 24. ORGANOSILANE REDUCTION OF HYDROXYLIMINES

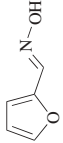
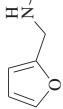




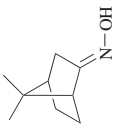
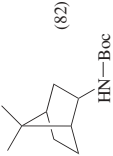
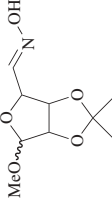
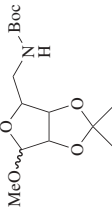

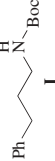


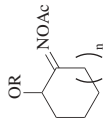

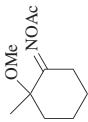
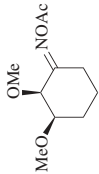
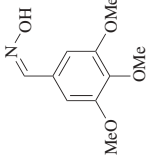
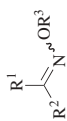
Hydroxyimine	Conditions	Product(s) and Yield(s) (%)	Refs.
	PMHS (3 eq), (<i>i</i> -BuCO) ₂ O (1.1 eq), 10% Pd-C, 40-50°, 3 h	 (65)	548
	PMHS (3 eq), (<i>i</i> -BuCO) ₂ O (1.1 eq), 10% Pd-C, 40-50°, 3 h	 (85)	548
	PMHS (3 eq), (<i>i</i> -BuCO) ₂ O (1.1 eq), 10% Pd-C, 40-50°, 4 h	 (90)	548
	PMHS (3 eq), (<i>i</i> -BuCO) ₂ O (1.1 eq), 10% Pd-C, 40-50°, 5 h	 (82)	548
	PMHS (3 eq), (<i>i</i> -BuCO) ₂ O (1.1 eq), 10% Pd-C, 40-50°, 6 h	 (85)	548
	PMHS (3 eq), (<i>i</i> -BuCO) ₂ O (1.1 eq), 10% Pd-C, 40-50°, 4 h	 (80)	548
	PMHS (3 eq), (<i>i</i> -BuCO) ₂ O (1.1 eq), 10% Pd-C, 40-50°, 3 h	 (75)	548

TABLE 24. ORGANOSILANE REDUCTION OF HYDROXYLIMINES (Continued)

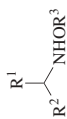
Hydroxyimine	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C_{9,15}</p>  <p>OR</p> <p>NOAc</p> <p>(CH₂)_n</p> <p>R n</p> <p>Me 1</p> <p>Me 3</p> <p>Bn 1</p> <p>Me 7</p>	<p>Et₃SiH (1.2 eq), TMSOTf (0.1 eq), CH₂Cl₂</p> <p>Temp Time</p> <p>0° 6 h</p> <p>rt 10 h</p> <p>0° 2 h</p> <p>0° 2 h</p>	<p>OR</p> <p>(CH₂)_n CN</p> <p>(65)</p> <p>(80)</p> <p>(66)</p> <p>(78)</p>	552
<p>C₁₀</p>  <p>N=OBz</p> <p>t-Bu</p>	Et ₃ SiH, TFA	<p>NHOBz</p> <p>t-Bu</p> <p>I</p> <p>I + II (85), III = 5:1</p> <p>II</p> <p>(81)</p>	550
 <p>OMe</p> <p>NOAc</p>	Et ₃ SiH (1.2 eq), TMSOTf (0.1 eq), CH ₂ Cl ₂ , 0°, 2 h	<p>OMe</p> <p>(CH₂)_n CN</p> <p>(82)</p>	552
 <p>OMe</p> <p>NOAc</p>	Et ₃ SiH (1.2 eq), TMSOTf (0.1 eq), CH ₂ Cl ₂ , rt, 9 h	<p>OMe</p> <p>(CH₂)_n CN</p> <p>(82)</p>	552
 <p>N=OH</p> <p>OMe</p> <p>OMe</p>	PMHS (3 eq), (t-BuCO ₂) ₂ O (1.1 eq), 10% Pd-C, 40-50°, 5 h	<p>NHOBz</p> <p>t-Bu</p> <p>I</p> <p>I + II (85), III = 5:1</p> <p>II</p> <p>(81)</p>	548

C₁₀₋₁₆

PhMe₂SiH (x eq),
TFA or TFA-CH₂Cl₂ (1:1)

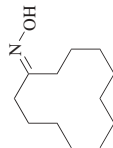
R ¹	R ²	R ³
Ph	Me	Ac
—(CH ₂) ₅ —	Bn	Bn
Ph	H	Bn
Ph	Me	Bz
<i>n</i> -C ₇ H ₁₅	Me	Bn

x	Temp	Time
1.2	rt	overnight
1.2	rt	24 h
1.2	rt	overnight
1.2	rt	overnight
2	50°	5 d

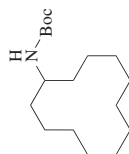


(67)
(65)
(75)
(78)
(23)

276, 551

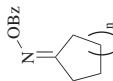
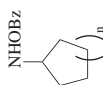
C₁₂

PMHS (3 eq), (*t*-BuCO)₂O (1.1 eq),
10% Pd-C, 40-50°, 7 h



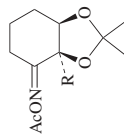
(80)

548

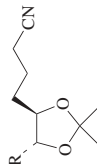
C₁₂₋₁₃Et₃SiH, TFA

n
1 (85)
2 (95)

550



Et₃SiH (1.2 eq), TMSOTf (0.1 eq),
CH₂Cl₂



R	Temp	Time
Me	rt	6 h (61)
Et	0°	4 h (81)

552

TABLE 24. ORGANOSILANE REDUCTION OF HYDROXYLIMINES (Continued)

Hydroxyimine	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₂₋₂₃</p> <p> R^1 R^2 $\text{—(CH}_2\text{)}_4\text{—}$ $\text{—(CH}_2\text{)}_5\text{—}$ $4\text{—MeC}_6\text{H}_4$ H Ph Me PhCH₂ Me $\text{—(CH}_2\text{)}_{11}\text{—}$ </p>	Et ₃ SiH, TFA, 0.5–6 h	<p>(85) (95) (54) (0) (90) (82) (85) cis:trans = 5:1</p>	550
<p>C₁₃</p>	PMHS (3 eq), (<i>r</i> -BuCO) ₂ O (1.1 eq), 10% Pd-C, 40–50°, 7 h	<p>(75)</p>	548
<p>C₁₃₋₂₀</p> <p> R $\text{—(CH}_2\text{)}_4\text{—}$ $\text{—(CH}_2\text{)}_5\text{—}$ $4\text{—MeC}_6\text{H}_4$ H Ph Me PhCH₂ Me $\text{—(CH}_2\text{)}_{11}\text{—}$ </p>	Et ₃ SiH (2 eq), TFA (as solvent), 40°, 12 h	<p>(66) (62) (79) (73) (79) (65) (54)</p>	553

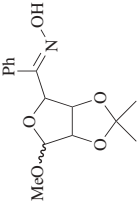
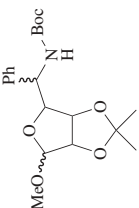
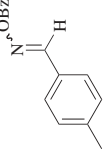
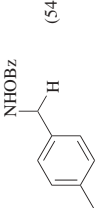
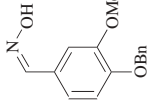
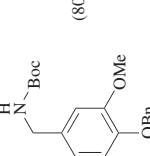
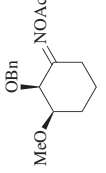
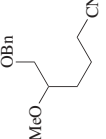
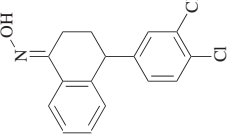
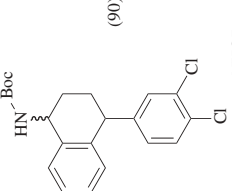

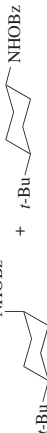
C ₁₅		PMHS (3 eq), <i>t</i> -BuCO ₂ O (1.1 eq), 10% Pd-C, 40-50°, 6 h		548
		Et ₃ SiH (2 eq), TFA		550
		PMHS (3 eq), <i>t</i> -BuCO ₂ O (1.1 eq), 10% Pd-C, 40-50°, 3 h		548
C ₁₆		Et ₃ SiH (1.2 eq), TMSOTf (0.1 eq), CH ₂ Cl ₂ , rt, 3 h		552
		PMHS (3 eq), <i>t</i> -BuCO ₂ O (1.1 eq), 10% Pd-C, 40-50°, 6 h		548
C ₁₇		Et ₃ SiH (2 eq), TFA		550
			I + II (85), II = 5:1	

TABLE 24. ORGANOSILANE REDUCTION OF HYDROXYLIMINES (Continued)

Hydroxyimine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₈	PhMe ₂ SiH (1.2 eq), TFA, rt	 I + II I + II (73), I:II = 99:1	551
C ₁₉	PhMe ₂ SiH (1.2 eq), TFA, rt	 I + II I + II (77), I:II = 25:75	551
	Et ₃ SiH (2 eq), TFA	 12 (73)	550
C ₃₅₋₄₂	PhMe ₂ SiH (2.3 eq), TFA	 12 (73)	549
C ₄₄	PhMe ₂ SiH (2.3 eq), TFA, 60°, 40 min	 12 (73)	549

TABLE 25. ORGANOSILANE REDUCTION OF NITROALKANES

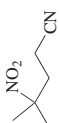

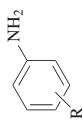
Nitro Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆	1. PhSiH ₃ (0.5 eq), (<i>n</i> -Bu) ₃ SnH (10%), ACHN (0.2 eq), MeC ₆ H ₅ , 110°, 5 h 2. ACHN (0.3 eq), MeC ₆ H ₅ , 110°, 3 h	 (67)	555
C _{6,9}	PMHS, Pd/C, EtOH, 80°	 (89)	316
	Et ₃ SiH (5 eq), (Ph ₃ P) ₃ RhCl (0.02 eq), MeC ₆ H ₅		554
	Time		
R	2 h	(86)	
H	2 h	(90)	
4-Me	4 h	(82)	
3,4-Me ₂	2 h	(83)	
2,4-Me ₂	3 h	(83)	
2,6-Me ₂	3 h	(85)	
3,5-Me ₂	6 h	(75)	
2,4,6-Me ₃	2 h	(86)	
4-MeO	2 h	(71)	
4-Cl	2 h	(—)	
4-Br	3 h	(—)	
4-CHO	3 h	(—)	
4-Ac	2 h	(71)	
3-Ac	2 h	(49)	
4-MeO ₂ C	2 h	(0)	
4-CN	2 h		

TABLE 25. ORGANOSILANE REDUCTION OF NITROALKANES (Continued)

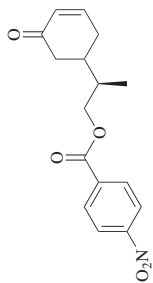
Nitro Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇ 	1. PhSiH ₃ (0.5 eq), (<i>n</i> -Bu) ₃ SnH (10%), AIBN (0.2 eq), MeC ₆ H ₅ , 110°, 5 h 2. AIBN (0.3 eq), MeC ₆ H ₅ , 110°, 3 h	EtO ₂ C-CH ₂ -CO ₂ Et (67)	555
C ₈ 	1. PhSiH ₃ (0.5 eq), (<i>n</i> -Bu) ₃ SnH (10%), ACHN (0.2 eq), MeC ₆ H ₅ , 110°, 5 h 2. ACHN (0.3 eq), MeC ₆ H ₅ , 110°, 3 h	(78)	555
	Et ₃ SiH (x eq), (Ph ₃ P) ₃ RhCl (y eq)	(73) (—) (76) (—) (82) (89) (78)	554
C ₁₀ 	1. PhSiH ₃ (0.5 eq), (<i>n</i> -Bu) ₃ SnH (10%), ACHN (0.2 eq), MeC ₆ H ₅ , 110°, 5 h 2. ACHN (0.3 eq), MeC ₆ H ₅ , 110°, 3 h	TBSO-CH ₂ -CH ₂ -CO ₂ Et (76)	555
C ₁₂ 	1. PhSiH ₃ (0.5 eq), (<i>n</i> -Bu) ₃ SnH (10%), ACHN (0.2 eq), MeC ₆ H ₅ , 110°, 5 h 2. ACHN (0.3 eq), MeC ₆ H ₅ , 110°, 3 h	(76)	555

C₁₃

1. PhSiH₃ (0.5 eq), (*n*-Bu)₃SnH (10%), ACHN (0.2 eq), MeC₆H₅, 110°, 5 h
2. ACHN (0.3 eq), MeC₆H₅, 110°, 3 h

(70)

555

C₁₆

- Et₃SiH (5 eq), (Ph₃P)₃RhCl (2 mol%), MeC₆H₅, reflux, 4 h

(—)

554

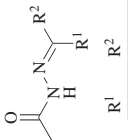
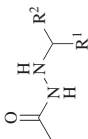


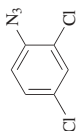
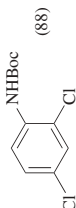
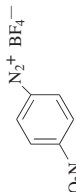
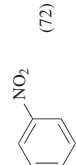
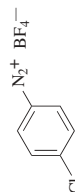
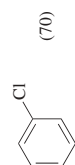
C₁₈

1. PhSiH₃ (0.5 eq), (*n*-Bu)₃SnH (10%), ACHN (0.2 eq), MeC₆H₅, 110°, 5 h
2. ACHN (0.3 eq), MeC₆H₅, 110°, 3 h

(71)

555

TABLE 26. ORGANOSILANE REDUCTION OF MISCELLANEOUS NITROGEN COMPOUNDS

Nitrogen Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{5,10}$ 	Et ₃ SiH (2 eq), TFA, 0°, 4 h		561
C_6 	PMHS (3 eq), 10% Pd-C, (Boc) ₂ O (1.1 eq), EtOH, rt, 5 h		557
	PMHS (3 eq), 10% Pd-C, (Boc) ₂ O (1.1 eq), EtOH, rt, 3 h		557
	Et ₃ SiH, MeCN, rt, 16 h		563
	Et ₃ SiH, MeCN, rt, 16 h		563

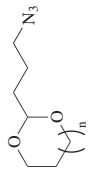


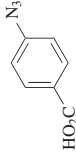
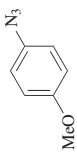
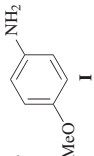
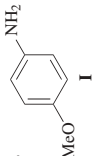
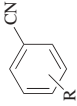
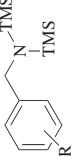
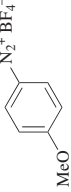
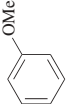
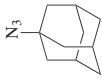
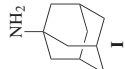

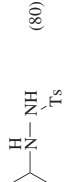
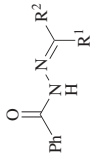
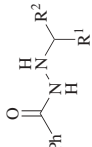
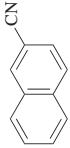
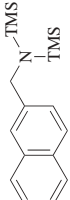
C _{6,13}	$\text{R}-\text{C}(\text{NEt}_3)^+\text{BF}_4^-$ <div> R <div> <i>c</i>-C₃H₅ <i>i</i>-Pr <i>n</i>-Bu <i>t</i>-Bu Ph Bn 1-C₁₀H₇ 1-Ad </div> </div>	Et ₃ SiH (2 eq), CH ₂ Cl ₂ , rt, 0.5-6 h	RCHO	28, 562
			(79)	
			(85)	
			(71)	
			(61)	
			(90)	
			(41)	
			(84)	
			(83)	
C _{7,8}		1. NOBF ₄ , SO ₂ 2. Et ₃ SiH	 <div> n <div> 1 (40) 2 (51) </div> </div>	779
C ₇		PMHS (3 eq), 10% Pd-C, (Boc) ₂ O (1.1 eq), EtOH, rt, 4 h	Ph-CH ₂ -NHBoc	557
		PMHS (3 eq), 10% Pd-C, (Boc) ₂ O (1.1 eq), EtOH, rt, 3 h	HO ₂ C-C ₆ H ₄ -NHBoc	557
		PhSiH ₃ (1.5-2 eq), [(<i>n</i> -Bu) ₃ Sn] ₂ O (0.025 eq), <i>n</i> -PrOH (2 eq), C ₆ H ₆ , AIBN (5 mol %), reflux, 90-120 min	 <div> I (94) </div>	556
		PMHS (1.5-2 eq), [(<i>n</i> -Bu) ₃ Sn] ₂ O (0.025 eq), <i>n</i> -PrOH (2 eq), C ₆ H ₆ , AIBN (5 mol %), reflux, 90-120 min	 <div> I (91) </div>	556

TABLE 26. ORGANOSILANE REDUCTION OF MISCELLANEOUS NITROGEN COMPOUNDS (Continued)

Nitrogen Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C ₇₋₉		TMSh (10 eq), Co ₂ (CO) ₈ (0.08-0.25 eq), CO, -20°		H (61)	559
				4-Me (91)	
C _{7,14}	$\text{R}-\text{N}^+\text{Pr}_i\text{FeCl}_4^-$	Et ₃ SiH (1.5 eq), CH ₂ Cl ₂ , rt, 0.5-6 h	RCHO	3-Me (57)	28
				2-Me (11)	
				4-MeO (88)	
				4-Cl (53)	
				4-NCCH ₂ (36)	
				4-Me ₂ N (73)	
				4-MeO ₂ C (46)	
				R	
				c-C ₃ H ₅ (77)	
				Ph (87)	
				4-ClC ₆ H ₄ (53)	
				4-O ₂ NC ₆ H ₄ (97)	
C ₇		Et ₃ SiH, MeCN, rt, 16 h		4-MeC ₆ H ₄ (88)	563
				4-MeOC ₆ H ₄ (57)	
				4-NCC ₆ H ₄ (19) ^a	
				4-OHCC ₆ H ₄ (78) ^a	
				4-AcC ₆ H ₄ (0)	
				PhCH=CH (56)	
				2-EtO ₂ CC ₆ H ₄ (42)	
				1-Ad (91)	
				(25)	
				(90)	

		Et_3SiH , THF, reflux, 2 h		563
		Et_3SiH , CH_2Cl_2 , reflux, 2 h		563
		PMHS (3 eq), 10% Pd-C, (Boc) $_2$ O (1.1 eq), EtOH, rt, 4 h		557
		PMHS (3 eq), 10% Pd-C, (Boc) $_2$ O (1.1 eq), EtOH, rt, 4 h		557
		PMHS (3 eq), 10% Pd-C, (Boc) $_2$ O (1.1 eq), EtOH, rt, 4 h		557
		PMHS (2 eq), $(\text{Ph}_3\text{P})_4\text{Pd}$ (0.01 eq), THF, rt, 3-5 h		270
		Et_3SiH (1.2 eq), CH_2Cl_2 , rt, 0.5-6 h		28

TABLE 26. ORGANOSILANE REDUCTION OF MISCELLANEOUS NITROGEN COMPOUNDS (Continued)

Nitrogen Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₁₀</div> 	1. PhSiH ₃ (1.5-2 eq), [(<i>n</i> -Bu) ₃ Sn] ₂ O (0.025 eq), <i>n</i> -PrOH (2 eq), C ₆ H ₆ 2. AIBN (5 mol%), reflux, 90-120 min	 I (99)	556
	1. PMHS (1.5-2 eq), [(<i>n</i> -Bu) ₃ Sn] ₂ O (0.025 eq), <i>n</i> -PrOH (2 eq), C ₆ H ₆ 2. AIBN (5 mol%), reflux, 90-120 min	I (96)	556
	Et ₃ SiH (2 eq), TFA, 0°, 1 h	 (80)	560
<div>C₁₀₋₁₅</div> 	Et ₃ SiH (2 eq), TFA, 0°, 4 h	 (86) (91) (80) (92) (82) (78) (79) (46)	561
<div>C₁₁</div> 	TMSH (10 eq), Co ₂ (CO) ₈ (0.08 eq), CO, -20°	 (64)	559


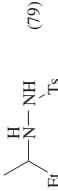
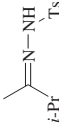
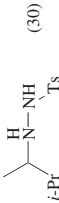
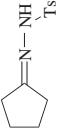

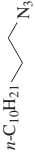
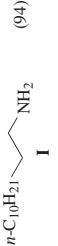
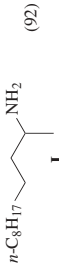
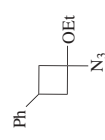
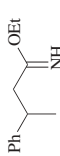
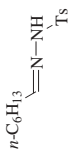
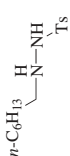
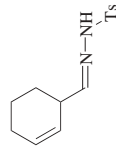
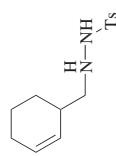
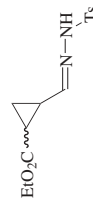
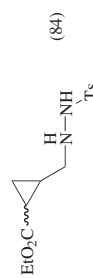
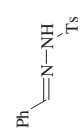
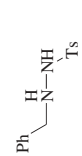

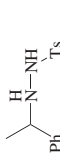
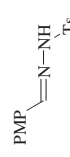
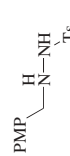
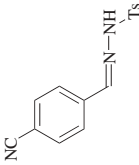
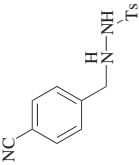
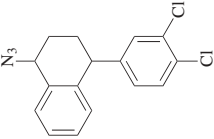
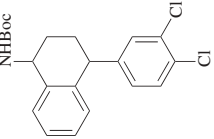
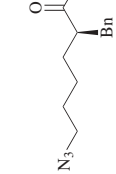
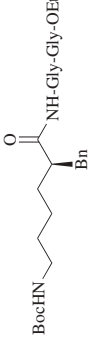
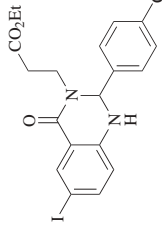
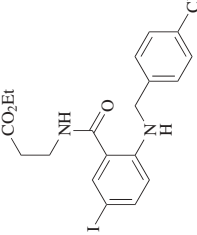
			560
C ₁₂			
			560
			560
			556
	1. PhSiH ₃ (1.5-2 eq), [(<i>n</i> -Bu) ₃ Sn] ₂ O (0.025 eq), <i>n</i> -PrOH (2 eq), C ₆ H ₆ 2. AIBN (5 mol%), reflux, 90-120 min		
	1. PMHS (1.5-2 eq), [(<i>n</i> -Bu) ₃ Sn] ₂ O (0.025 eq), <i>n</i> -PrOH (2 eq), C ₆ H ₆ 2. AIBN (5 mol%), reflux, 90-120 min	I (95)	556
	1. PhSiH ₃ (1.5-2 eq), [(<i>n</i> -Bu) ₃ Sn] ₂ O (0.025 eq), <i>n</i> -PrOH (2 eq), C ₆ H ₆ 2. AIBN (5 mol%), reflux, 90-120 min		556
	1. PMHS (1.5-2 eq), [(<i>n</i> -Bu) ₃ Sn] ₂ O (0.025 eq), <i>n</i> -PrOH (2 eq), C ₆ H ₆ 2. AIBN (5 mol%), reflux, 90-120 min	I (94)	556

TABLE 26. ORGANOSILANE REDUCTION OF MISCELLANEOUS NITROGEN COMPOUNDS (Continued)

Nitrogen Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	$PhSiH_3$, (<i>n</i> -Bu) $_3$ SnH (cat.), <i>n</i> -PrOH, AIBN, 80°	 (—)	556
C_{14} 	Et_3SiH (2 eq), TFA, 0°, 1 h	 (75)	560
	Et_3SiH (2 eq), TFA, 0°, 1 h	 (82)	560
	Et_3SiH (2 eq), TFA, 0°, 1 h	 (84)	560
	Et_3SiH (2 eq), TFA, 0°, 1 h	 (82)	560
C_{15} 	Et_3SiH (2 eq), TFA, 0°, 1 h	 (51)	560
	Et_3SiH (2 eq), TFA, 0°, 1 h	 (81)	560

				560
Et_3SiH (2 eq), TFA, 0° , 1 h				
				557
PMHS (3 eq), 10% Pd-C, (Boc) ₂ O (1.1 eq), EtOH, rt, 5 h				
				558
Et_3SiH , 20% Pd(OH) ₂ C, (Boc) ₂ O				
				780
Et_3SiH , TFA, 0° to rt, 24 h				

^a The yield was determined by gas chromatography.

TABLE 27. ORGANOSILANE REDUCTION OF MISCELLANEOUS SULFUR COMPOUNDS

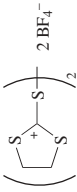


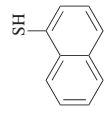

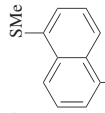
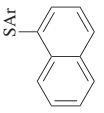
Sulfur Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	Et_3SiH (1 eq), MeCN, <5 min	 (100)	565
C_{8-14} 	Et_3SiH (1.4 eq), TFA, 60°, 25 h	<div> <div>R</div> <div> $n-Bu$ (67) Ph (45) Ph (52) $2-O_2NC_6H_4$ (0) $2,4-(O_2N)_2C_6H_3$ (0) $4-MeOC_6H_4$ (74) </div> </div>	564
C_{10} 	Et_3SiH (1.3 eq), $BF_3 \cdot OH_2$ (4-6 eq), CH_2Cl_2 , rt, 6 h		217
C_{11-12} 	Et_3SiH (3-5 eq), $BF_3 \cdot OEt_2$, CH_2Cl_2 , 0°	<div> <div>R</div> <div> <div>Time</div> <div> H 24 h (20) SMe 92 h (70) </div> </div> </div>	263
C_{16-20} 	Et_3SiH (3-5 eq), $BF_3 \cdot OEt_2$, CH_2Cl_2 , 0°, 20 h	<div> <div>Ar</div> <div> <div>Time</div> <div> Ph 20 h (30) Bn 168 h (40) $1-Np$ 20 h (50) $2-Np$ 22 h (25) </div> </div> </div>	263

TABLE 28. ORGANOSILANE REDUCTION OF SMALL RING COMPOUNDS






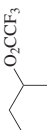









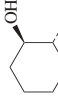

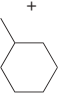







Small Ring Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	HMe ₂ SiOSiMe ₂ H (1.0 eq), I ₂ (cat.), CH ₂ Cl ₂ , rt, 10 min	 (90)	357
	Et ₃ SiH (1 eq), TFA (x eq), 20°	 I +  II +  III +  IV +  V +  VI +  VII +  VIII + IX + X + XI + XII + XIII + XIV + XV + XVI + XVII + XVIII + XIX + XX + XXI + XXII + XXIII + XXIV + XXV + XXVI + XXVII + XXVIII + XXIX + XXX + XXXI + XXXII + XXXIII + XXXIV + XXXV + XXXVI + XXXVII + XXXVIII + XXXIX + XL + XLI + XLII + XLIII + XLIV + XLV + XLVI + XLVII + XLVIII + XLIX + L + LI + LII + LIII + LIV + LV + LVI + LVII + LVIII + LIX + LX + LXI + LXII + LXIII + LXIV + LXV + LXVI + LXVII + LXVIII + LXIX + LXX + LXXI + LXXII + LXXIII + LXXIV + LXXV + LXXVI + LXXVII + LXXVIII + LXXIX + LXXXX + LXXXXI + LXXXXII + LXXXXIII + LXXXXIV + LXXXXV + LXXXXVI + LXXXXVII + LXXXXVIII + LXXXXIX + LXXXXX + LXXXXXI + LXXXXXII + LXXXXXIII + LXXXXXIV + LXXXXXV + LXXXXXVI + LXXXXXVII + LXXXXXVIII + LXXXXXIX + LXXXXXX + LXXXXXXI + LXXXXXXII + LXXXXXXIII + LXXXXXXIV + LXXXXXXV + LXXXXXXVI + LXXXXXXVII + LXXXXXXVIII + LXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII + LXXXXXXXIII + LXXXXXXXIV + LXXXXXXXV + LXXXXXXXVI + LXXXXXXXVII + LXXXXXXXVIII + LXXXXXXXIX + LXXXXXXX + LXXXXXXXI + LXXXXXXXII +	

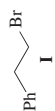
TABLE 28. ORGANOSILANE REDUCTION OF SMALL RING COMPOUNDS (Continued)

Small Ring Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₆	Et ₃ SiH, BF ₃ , CH ₂ Cl ₂ , several weeks	(—)	566
	HMMe ₂ SiOSiMe ₂ H (1.0 eq), NaI (1.3 eq), CH ₂ Cl ₂ , 5–10°, 30 min	 I (75)	357
	HMMe ₂ SiOSiMe ₂ H (1.0 eq), I ₂ (cat.), CH ₂ Cl ₂ , rt, 10 min	 I (100)	357
	PMHS (1 eq), NaI (1.33 eq), TMSCl (1.5 eq), MeCN, reflux, 30 min	 I (75)	567
	PMHS (1 eq), LiBr (1.33 eq), TMSiCl (1.5 eq), MeCN, reflux, 7 h	 (93)	567
 C ₇	Et ₃ SiH (1 eq), TFA (x eq), 20°, 140 h	 I +  II +  III +  IV	229
	Et ₃ SiH (1 eq), TFA (2 eq), 20°	 I +  II	229
	Et ₃ SiH (1 eq), TFA (2 eq), 20°	 I +  II	229



567

(69)



PMHS (1 eq), LiBr (1.33 eq),
TMSCl (1.5 eq), HOAc, reflux, 15 min

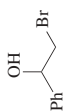
357

I (69)

HMe₂SiOSiMe₂H (1.0 eq),
LiBr (1.3 eq), TFA, 5-10°, 15 h

357

(69)



HMe₂SiOSiMe₂H (1.0 eq),
LiBr (1.3 eq), TFA, 5-10°, 1.5 h

567

(76)



PMHS (1 eq), NaI (1.33 eq),
TMSCl (1.5 eq), MeCN, reflux, 45 min

357

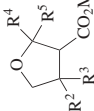
I (76)

HMe₂SiOSiMe₂H (1.0 eq),
NaI (1.3 eq), CH₂Cl₂, 5-10°, 45 min

357

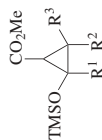
I (62)

HMe₂SiOSiMe₂H (1.0 eq), I₂ (1.6 eq),
CH₂Cl₂, rt, 10 min



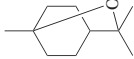
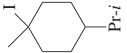
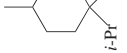


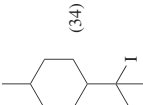



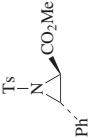
1. LDA/THF; R¹R²CO; TBAF^a
2. Et₃SiH (1.1 eq), BF₃•OEt₂ (1.1 eq),
CH₂Cl₂, -78°, 45 min, rt, 3 h

C₉,²⁰



R ¹	R ²	R ³	R ⁴	R ⁵	cis:trans	
H	Me	Me	Me	H	(51)	1:3
H	Me	Me	Me	Me	(71)	—
H	—(CH ₂) ₃ —	Me	H	H	(54)	1:1
H	—(CH ₂) ₃ —	—(CH ₂) ₃ —	Me	Me	(48)	—
—(CH ₂) ₄ —	H	Me	Me	Me	(66)	>9:1
H	Me	Me	Ph	H	(79)	2:3
Ph	H	H	Me	Me	(54)	1:1
H	Me	Me	PhMeCH	H	(71)	1:2
H	Me	Me	Ph	Ph	(47)	—

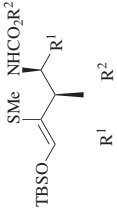
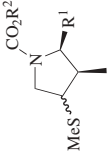
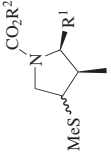
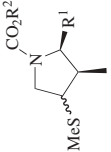
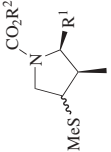
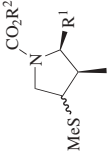
TABLE 28. ORGANOSILANE REDUCTION OF SMALL RING COMPOUNDS (Continued)

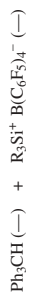
Small Ring Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	HMe ₂ SiOSiMe ₂ H (1.0 eq), NaI (1.3 eq), CH ₂ Cl ₂ , 5-10°, 20 min	 I +  II I + II (80), I:II 57:43	357, 567
C ₁₁ 	PMHS (1 eq), NaI (1.33 mol%), TMSCl (1.5 eq), MeCN, reflux, 7 h	 I (46) +  (34)	567
C ₁₄ 	PMHS (xs), EtOH, Pd-C, rt, 6 h	EtO ₂ C—CH ₂ —CH ₂ —NHTs (80)	568
C ₁₅ 	Et ₃ SiH (3.9 eq), BF ₃ , CH ₂ Cl ₂ , 20°, 7 d	Ph—CH ₂ —CH ₂ —CH ₂ —Ph (100)	566
C ₁₆ 	PMHS (xs), EtOH, Pd-C, 6 h	Ph—CH ₂ —CH ₂ —NHTs (96)	568
C ₁₇ 	PMHS (xs), EtOH, Pd-C, rt, 6 h	Ph—CH ₂ —CH ₂ —CH ₂ —NHTs (60)	568
		Ph—CH ₂ —CH ₂ —NHTs CO ₂ Me (95)	568

C ₁₉		PMHS (xs), EtOH, Pd-C, rt, 6 h		568
C ₂₀		PMHS (xs), EtOH, Pd-C, rt, 6 h		568
C ₂₁		PMHS (xs), EtOH, Pd-C, rt, 6 h		568
C ₂₃		PMHS (xs), EtOH, Pd-C, rt, 6 h		568
C ₂₄		PMHS (xs), EtOH, Pd-C, rt, 6 h		568
		Et ₃ SiR (1.1 eq), TFA (2.6 eq), CH ₂ Cl ₂ , 20°, 30 h		781
				568

^a These sequential steps generate the intermediate substituted tetrahydrofuran-2-ol, which is converted in the second sequence into the final product shown.

TABLE 29. MISCELLANEOUS ORGANOSILANE REDUCTIONS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₁₈₋₂₀</div> <div>  </div>	Et ₃ SiH, TFA, MeCN	<div>  </div>	782
		(95)	
		(95)	
		(90)	
<div>C₁₉</div> <div>  </div>	TMSh (0.8 eq), rt, 0.5 h	Ph ₃ CH (100) + Me ₂ SiF (100)	62
	Et ₃ SiH (0.8 eq), rt, 1.5 h	Ph ₃ CH (100) + Et ₃ SiF (100)	62
	Me ₂ SiH ₂ (0.8 eq) rt, 0.5 h	Ph ₃ CH (100) + Me ₂ SiHF (100)	62
	Me ₂ SiH ₂ (0.45 eq), rt, 8 h	Ph ₃ CH (100) + Me ₂ SiF ₂ (95)	62
	Et ₂ SiH ₂ (0.80 eq), rt, 1.5 h	Ph ₃ CH (100) + Et ₂ SiHF (100)	62
<div>C₂₀</div> <div>  </div>	<div>  </div>	<div>  </div>	60
	(<i>i</i> -Pr) ₃ SiH, MeCN	Ph ₃ CH + [(<i>i</i> -Pr) ₃ Si-NCMe][Br ₅ -CB ₉ H ₅] (—)	46
	(<i>i</i> -Pr) ₃ SiH, MeC ₆ H ₅	Ph ₃ CH + [(<i>i</i> -Pr) ₃ Si][Br ₅ -CB ₉ H ₅] (—)	46



R ₃ SiH	Solvent	
	R ₃ Si	Solvent
TMS		C ₆ D ₆
Et ₃ Si		C ₆ D ₆
Et ₃ Si		MeC ₆ H ₅
Et ₃ Si		MeCN
(<i>i</i> -Pr) ₃ Si		C ₆ D ₆
(TMS) ₃ Si		C ₆ D ₆

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES













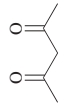
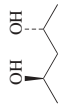
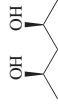
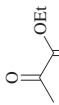
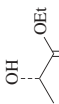
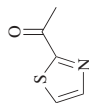
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	Ph_2SiH_2 (4 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1.0 mol%), 23 (1.1 mol%), 0° , DME, 26 h	 +  I + II (94), I:II 90:10, I = 96% ee	577
	$\text{Me}(\text{EtO})_2\text{SiH}$ (1.43 eq), 197 (0.57 mol%), MeLi (1.14 mol%), THF, rt	 I	583
C_{4-8} 	$[-(\text{Me})(\text{H})\text{Si}(\text{O}-)]_4$ (1.43 eq), 197 (0.57 mol%), MeLi (1.14 mol%), THF, rt	 I	583
	$[-(\text{Me})(\text{H})\text{Si}(\text{O}-)]_4$ (1.43 eq), 197 (0.57 mol%), MeLi (1.14 mol%), THF, rt	 I	583
C_{4-8} 	$\text{Me}(\text{EtO})_2\text{SiH}$ (3.75 eq), 197 (0.57 mol%), <i>n</i> -BuLi (1.14 mol%), THF, rt	 I	583
	$\text{Me}(\text{EtO})_2\text{SiH}$ (3.75 eq), 197 (0.57 mol%), <i>n</i> -BuLi (1.14 mol%), THF, rt	 I	583

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																						
C ₄₋₁₂ 	Ph ₂ SiH ₂ (1.1 eq), [Rh(cod)Cl] ₂ (0.5 mol%), 107 (1.2 mol%)		575																																																																						
C ₅		<table><tr><th>R¹</th><th>R²</th><th>Temp</th><th>Time</th><th>% ee</th></tr><tr><td>Et</td><td>Me</td><td>0°</td><td>24 h</td><td>(—)</td></tr><tr><td><i>i</i>-Pr</td><td>Me</td><td>0°</td><td>24 h</td><td>(—)</td></tr><tr><td><i>t</i>-Bu</td><td>Me</td><td>0°</td><td>96 h</td><td>(—)</td></tr><tr><td>EtO₂C(CH₂)₂</td><td>Me</td><td>0°</td><td>24 h</td><td>(86)</td></tr><tr><td><i>n</i>-C₆H₁₃</td><td>Me</td><td>0°</td><td>40 h</td><td>(89)</td></tr><tr><td><i>c</i>-C₆H₁₁</td><td>Me</td><td>0°</td><td>24 h</td><td>(82)</td></tr><tr><td>Ph</td><td>Me</td><td>0°</td><td>24 h</td><td>(89)</td></tr><tr><td>Ph</td><td>ClCH₂</td><td>20°</td><td>24 h</td><td>(89)</td></tr><tr><td>Ph</td><td>Et</td><td>0°</td><td>24 h</td><td>(81)</td></tr><tr><td>Ph</td><td><i>i</i>-Pr</td><td>20°</td><td>24 h</td><td>(87)</td></tr><tr><td>Ph</td><td><i>t</i>-Bu</td><td>20°</td><td>24 h</td><td>(69)</td></tr><tr><td>1-C₁₀H₇</td><td>Me</td><td>0°</td><td>24 h</td><td>(81)</td></tr><tr><td>2-C₁₀H₇</td><td>Me</td><td>0°</td><td>24 h</td><td>(87)</td></tr></table>	R ¹	R ²	Temp	Time	% ee	Et	Me	0°	24 h	(—)	<i>i</i> -Pr	Me	0°	24 h	(—)	<i>t</i> -Bu	Me	0°	96 h	(—)	EtO ₂ C(CH ₂) ₂	Me	0°	24 h	(86)	<i>n</i> -C ₆ H ₁₃	Me	0°	40 h	(89)	<i>c</i> -C ₆ H ₁₁	Me	0°	24 h	(82)	Ph	Me	0°	24 h	(89)	Ph	ClCH ₂	20°	24 h	(89)	Ph	Et	0°	24 h	(81)	Ph	<i>i</i> -Pr	20°	24 h	(87)	Ph	<i>t</i> -Bu	20°	24 h	(69)	1-C ₁₀ H ₇	Me	0°	24 h	(81)	2-C ₁₀ H ₇	Me	0°	24 h	(87)	
R ¹	R ²	Temp	Time	% ee																																																																					
Et	Me	0°	24 h	(—)																																																																					
<i>i</i> -Pr	Me	0°	24 h	(—)																																																																					
<i>t</i> -Bu	Me	0°	96 h	(—)																																																																					
EtO ₂ C(CH ₂) ₂	Me	0°	24 h	(86)																																																																					
<i>n</i> -C ₆ H ₁₃	Me	0°	40 h	(89)																																																																					
<i>c</i> -C ₆ H ₁₁	Me	0°	24 h	(82)																																																																					
Ph	Me	0°	24 h	(89)																																																																					
Ph	ClCH ₂	20°	24 h	(89)																																																																					
Ph	Et	0°	24 h	(81)																																																																					
Ph	<i>i</i> -Pr	20°	24 h	(87)																																																																					
Ph	<i>t</i> -Bu	20°	24 h	(69)																																																																					
1-C ₁₀ H ₇	Me	0°	24 h	(81)																																																																					
2-C ₁₀ H ₇	Me	0°	24 h	(87)																																																																					
	Ph ₂ SiH ₂ (2.5 eq), [Rh(cod) ₂]BF ₄ (1.0 mol%), 23 (1.1 mol%), −30°, THF, 75 h	 I +  II	I + II (45), III = 42.58, I = 35% ee	577																																																																					
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1.0 mol%), 23 (1.1 mol%), 0°, THF, 4 h		(60) 80% ee	577																																																																					



C_{5,17}



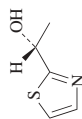
C₆



PMHS (4 eq), CuCl/NiOBu-*t* (1 mol%),
catalyst (0.05 mol%), MeC₆H₅, 4 h

Catalyst	Temp	Time
124	-50°	4 h
121	-78°	—

PMHS, Sn(OTf)₂ (10 mol%),
85 (10 mol%), MeOH, rt, 12-14 h



% ee	
(97)	90
(—)	90

R ¹	R ²	
OH	CF ₃	(75)
R ¹ -R ²	Me	(98)
Ph	CO ₂ Me	(99)
Ph	CO ₂ Et	(99)
Ph	CO ₂ Et	(99)
4-MeOC ₆ H ₄	CO ₂ Me	(99)
4-MeC ₆ H ₄	CO ₂ Me	(96)
4-O ₂ NC ₆ H ₄	CO ₂ Me	(98)
1-C ₁₀ H ₇	CO ₂ Me	(98)
2-C ₁₀ H ₇	CO ₂ Me	(96)
Ph	CH ₂ - <i>N</i> -phth	(98)
4-MeC ₆ H ₄	CH ₂ - <i>N</i> -phth	(88)
4-ClC ₆ H ₄	CH ₂ - <i>N</i> -phth	(89)
4-O ₂ NC ₆ H ₄	CH ₂ - <i>N</i> -phth	(50)
2-C ₄ H ₉ S	CO ₂ Et	(98)



(75) 98% ee





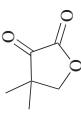
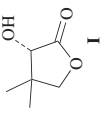
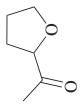
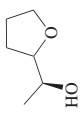
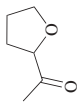
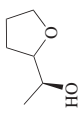
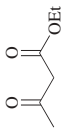
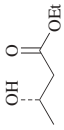
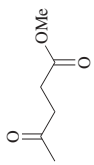
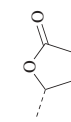
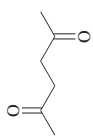
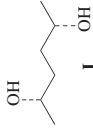
I (30) 53% ee

I (58) 2% ee



75% conversion, 20% ee^b

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)			Refs.
		R	Opt. Yield	Conf.	
	Et_3SiH_2 , $[(\text{-})(\text{-})\text{-bmpp}]_2\text{RhCl}$, C_6H_6 , 5–50°, 3–48 h				785, 786
	Ph_2SiH_2 (1.1 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.5 mol%), 108 (1.2 mol%), THF, 0°, 120 h		(76)	84% ee	575
	Ph_2SiH_2 (1 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.3 mol%), 44 (0.4 mol%), THF, rt, 30 min		I (68)	37% ee	787
	PMHS (1.1 eq), Et_2Zn (20 mol%), (<i>R,R</i>)-ebpe (20 mol%), vitride (3%), MeC_6H_5 , rt, 24 h		(—)	66% ee	594
	Ph_2SiH_2 (1.5 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1.0 mol%), 23 (1.1 mol%), –30°, THF, 14 h		(43)	32% ee	577
	Ph_2SiH_2 (1.5 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1.0 mol%), 23 (1.1 mol%), –30°, THF, 31 h		(74)	88% ee	577
	Ph_2SiH_2 (2.5 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1.0 mol%), 23 (1.1 mol%), –30°, DME, 30 h		I + II (97)	I:II = 75:25, I = 97% ee	577

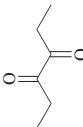
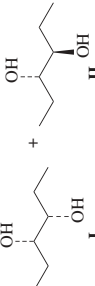
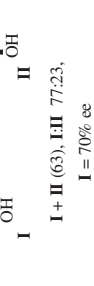
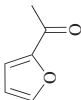

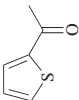

	Ph_2SiH_2 (2.5 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1.0 mol%), 23 (1.1 mol%), 0°, DME, 55 h		577																								
																											
		I + II (63), I:II 77:23, I = 70% ee																									
	PMHS (4 eq), $\text{CuCl}/\text{NaOBu-}t$ (1 mol%), 124 (0.05 mol%), MeC_6H_5 , -50°, 5 h		590																								
		(85) 92% ee																									
	PMHS (4 eq), $\text{CuCl}/\text{NaOBu-}t$ (1 mol%), 121 (0.05 mol%), MeC_6H_5 , -78°	I (—) 90% ee	590																								
	PMHS (4 eq), $\text{CuCl}/\text{NaOBu-}t$ (1 mol%), 122 (0.05 mol%), MeC_6H_5 , -78°	I (—) 78% ee	590																								
	PMHS (4 eq), ligand (3 mol%), CuCl (3 mol%), $\text{NaOBu-}t$ (3 mol%), THF (x%), MeC_6H_5 [(100 - x)]%	I (—)	590																								
		<table><tr><th>Ligand</th><th>x</th><th>% ee</th></tr><tr><td>124</td><td>0</td><td>91</td></tr><tr><td>121</td><td>0</td><td>90</td></tr><tr><td>121</td><td>12.5</td><td>88</td></tr><tr><td>121</td><td>100</td><td>70</td></tr><tr><td>122</td><td>0</td><td>78</td></tr><tr><td>122</td><td>12.5</td><td>74</td></tr><tr><td>122</td><td>100</td><td>67</td></tr></table>	Ligand	x	% ee	124	0	91	121	0	90	121	12.5	88	121	100	70	122	0	78	122	12.5	74	122	100	67	
Ligand	x	% ee																									
124	0	91																									
121	0	90																									
121	12.5	88																									
121	100	70																									
122	0	78																									
122	12.5	74																									
122	100	67																									
	PMHS (1.2 eq), Ph_2Zn (2 mol%), 131 (2 mol%), MeC_6H_5 , rt, 4 h		788																								
		(>99) 78% ee																									

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions		Product(s) and Yield(s) (%)		Refs.
	Ar	R	Time	% ee	
C ₆ -11 <div></div>	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod)Cl] ₂ (2.5 mol%), 29 (5 mol%), THF, 0°				
	Ar	R	Time		
	2-C ₄ H ₉ S	Me	96 h	(100)	78
	Ph	Me	24 h	(3)	85
	Ph	Et	70 h	(14)	58
	Ph	CH ₂ Cl	120 h	(85)	88
	Ph	CO ₂ Me	25 h	(31)	60
	Ph	<i>t</i> -Bu	240 h	(5)	85
	1-indanone		240 h	(5)	42
	4-O ₂ NC ₆ H ₄	Me	72 h	(45)	76
C ₆ -12 <div></div>	4-ClC ₆ H ₄	Me	72 h	(41)	74
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod)Cl] ₂ (2.5 mol%), 29 (5 mol%), MeOH, 0°				
	Ar	R	Time		
	2-C ₄ H ₉ S	Me	70 h	(100)	43
	Ph	Me	70 h	(46)	48
	Ph	Et	40 h	(28)	31
	Ph	CH ₂ Cl	70 h	(68)	25
	Ph	CO ₂ Me	25 h	(95)	41
	Ph	<i>t</i> -Bu	170 h	(11)	95
	1-indanone		170 h	(15)	31
4-O ₂ NC ₆ H ₄	Me	50 h	(92)	25	
4-ClC ₆ H ₄	Me	70 h	(51)	22	
4-MeC ₆ H ₄	Me	70 h	(0)	—	
4-MeOC ₆ H ₄	Me	70 h	(0)	—	
2-C ₁₀ H ₇	Me	70 h	(24)	37	

C_{6,11}



R₃SiH₄, [(+)-(R)-bmpp]₂RhCl, C₆H₆,
5-50°, 3-48 h

R ¹	R ²
Me	<i>i</i> -Bu
Me	<i>i</i> -Bu
Me	<i>n</i> -C ₆ H ₁₃
Me	<i>c</i> -C ₆ H ₁₁
<i>n</i> -Pr	<i>c</i> -C ₆ H ₁₁
<i>i</i> -Pr	<i>c</i> -C ₆ H ₁₁
<i>n</i> -Pr	<i>c</i> -C ₆ H ₁₁
<i>i</i> -Bu	<i>c</i> -C ₆ H ₁₁

C_{6,12}



Ph₂SiH₂ (1.6 eq), **87** (x mol%), **99** (10 mol%),
AgBF₄ (0.02 mol%), THF

R ¹	R ²
EtO ₂ CCH ₂	Me
EtO ₂ C(CH ₂) ₂	Me
AcO(CH ₂) ₃	Me
Me ₂ C=CHCH ₂ CH ₂	Me
<i>n</i> -C ₈ H ₁₃	Me
2-ClC ₆ H ₄	Me
Ph	Et
Bn	Me
2-MeO ₂ CC ₆ H ₄	Me
3-AcOC ₆ H ₄	Me
Ph	<i>n</i> -Pr
2-MeOBn	Me
BnCH ₂	Me
1-C ₁₀ H ₇	Me
2-C ₁₀ H ₇	Me








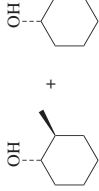
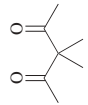
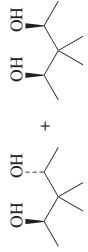


Opt.	Yield	Conf.
(98)	25	R
(99)	12	R
(98)	9	R
(92)	40	R
(98)	11	R
(94)	4	S
(95)	10	R
(90)	43	R



% ee	
(60)	27
(91)	95
(85)	68
(94)	70
(85)	63
(74)	94
(73)	91
(95)	71
(95)	96
(81)	92
(82)	82
(95)	82
(92)	66
(87)	94
(93)	93

580, 581

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6,12} 	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod)Cl] ₂ (0.25 mol %), 38 (0.5 mol %), Et ₂ O, rt, 15–25 h	 % ee Conf. (100) 87 R (45) 89 R (100) 91 R (19) 8 S (12) 23 S (92) 60 R (99) 88 R	571
C₇ 	1. Ph ₂ SiH ₂ (0.1 eq), 197 (2 mol %), pyrrolidine, MeOH, THF, 60° 2. PMHS, ketone, MeOH (3–7 eq), 15°, 11 h	 (92) 50% ee	587
	Ph ₂ SiH ₂ (1.3 eq), RhCl ₃ (1 mol %), 197 (5 mol %), AgBF ₄ (2 mol %), THF, 0°, 1 d	 I + II (88), I:II = 41:59 I 1S, 2S 91% ee II 1S, 2R 89% ee	390
	Ph ₂ SiH ₂ (2.5 eq), [Rh(cod) ₂]BF ₄ (1.0 mol %), 23 (1.1 mol %), –30°, THF, 75 h	 I + II (45), I:II = 42:58, I = 35% ee	577
	Ph ₂ SiH ₂ (2.5 eq), [Rh(cod) ₂]BF ₄ (1.0 mol %), 23 (1.1 mol %), –30°, THF, 94 h	 I + II (75), I:II = 69:31, II = 89% ee	577

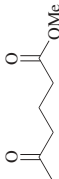
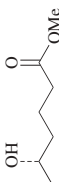
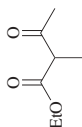
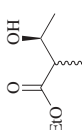
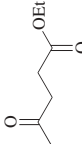
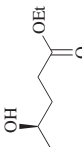
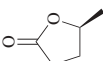
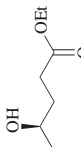
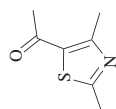
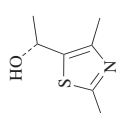
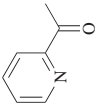
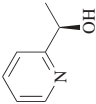
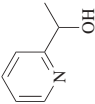
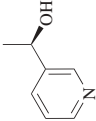
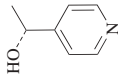

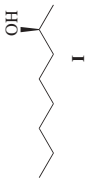
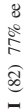
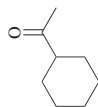
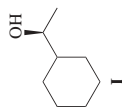
	Ph_2SiH_2 (1.5 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1.0 mol%), 23 (1.1 mol%), -30° , THF, 425 h		(74) 69% ee ^b	577																				
	$\text{Ph}(\text{1-Np})\text{SiH}_2$ (1.5 eq), $[\text{Rh}(\text{cod})]\text{SbF}_6$ (1 mol%), 126 (1 mol%), THF, -20°		(80) 98% ee, syn:anti = 1:1	576																				
	Ph_2SiH_2 (1 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.3 mol%), 108 (0.4 mol%), THF, rt, 30 min		(66) 52% ee	787																				
	Ph_2SiH_2 (1.1 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.5 mol%), 108 (1.2 mol%), THF, 0° , 24 h		(71) 74% ee	575																				
	Ph_2SiH_2 (1.6 eq), 87 (4.0 mol%), complex (10 mol%), AgBF_4 (0.02 mol%), THF			580																				
		<table><tr><th>Complex</th><th>Temp</th><th>Time</th><th>% ee</th></tr><tr><td>100</td><td>0°</td><td>7 h</td><td>(82) 94</td></tr><tr><td>101</td><td>10°</td><td>18 h</td><td>(79) 79</td></tr><tr><td>103</td><td>10°</td><td>4 h</td><td>(80) 75</td></tr><tr><td>104</td><td>30°</td><td>—</td><td>(0) —</td></tr></table>	Complex	Temp	Time	% ee	100	0°	7 h	(82) 94	101	10°	18 h	(79) 79	103	10°	4 h	(80) 75	104	30°	—	(0) —		
Complex	Temp	Time	% ee																					
100	0°	7 h	(82) 94																					
101	10°	18 h	(79) 79																					
103	10°	4 h	(80) 75																					
104	30°	—	(0) —																					
	PMHS (4 eq), 124 (0.05 mol%), CuCl (1 mol%), $\text{NaOBu-}t$ (1 mol%), THF/ MeC_6H_5 , -50° , 4 h		(94) 99% ee	590																				

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₇	PMHS (4 eq), 124 (0.05 mol%), CuCl (1 mol%), NaOBu- <i>t</i> (1 mol%), MeC ₆ H ₅ , -50°, 2 h	 (97) 90% ee	590
	PMHS, Sn(OTf) ₂ (10 mol%), 87 (10 mol%), MeOH, rt, 12-14 h	 (99) 0% ee	385
	PMHS (4 eq), 124 (0.05 mol%), CuCl (3 mol%), NaOBu- <i>t</i> (1 mol%), THF/MeC ₆ H ₅ , -35°, 8 h	 (92) 75% ee	590
	PMHS (4 eq), 124 (0.05 mol%), CuCl (3 mol%), NaOBu- <i>t</i> (1 mol%), THF/MeC ₆ H ₅ , -78°, 6.5 h	 (97) 84% ee	590
 C ₈	Ph ₂ SiH ₂ (1.5 eq), [Ir(cod)Cl] ₂ (0.25 mol%), 38 (0.5 mol%), Et ₂ O, 0°, 25 h	 (19) 19% ee	582
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1 mol%), 1 (1.1 mol%), THF, -50°, 48 h	 1 (82) 77% ee	578



PMHS (1.1 eq), Et₂Zn (20 mol%),
(*R,R*)-ebpe (20 mol%), vitride (3%),
MeC₆H₅, rt, 24 h



594

(—) 20% ee

1. Ph₂SiH₂ (0.1 eq), **197** (2 mol%), pyrrolidine,
MeOH, THF, 60°
2. PMHS, ketone, MeOH (3-7 eq), 15°, 6 h

I (>98) 23% ee

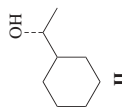
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Ph(1-Np)SiH₂ (1.5 eq),
[Rh(cod)]SbF₆ (1 mol%), **126** (1 mol%),
THF, -20°

I (90) 92% ee

576

Ph₂SiH₂ (1 eq), [Rh(cod)Cl]₂ (0.3 mol%),
46 (0.4 mol%), THF, rt, 30 min



788

Ph₂SiH₂ (1.25 eq), Rh[(NBD)Cl]₂ (0.5 %),
ligand (0.5 %), MeC₆H₅

I (—)

791

Ligand	Temp	% ee
116	0°	37
117	0°	33
118	10°	50
119	27°	49

Ph₂SiH₂ (1.5 eq), [Rh(cod)₂]BF₄ (1 mol%),
25 (1.1 mol%), THF, rt, 10 h

I (62) 80% ee



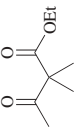
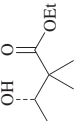



606

1. **197** (4.5 eq), *n*-BuLi (9 eq), C₆H₆
2. PMHS (5 eq)
3. Add ketone, 4 d

II (67) 24% ee

588

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1.0 mol %), 25 (1.1 mol %), -40°, THF, 26 h	 (70) 88% ee	577
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (0.5 mol %), 23 (1.1 mol %), -30°, THF, 24 h	 (80) 98% ee	577
	PMHS (1.2 eq), (<i>i</i> -Pr) ₂ Zn (2 mol %), 131 (2 mol %), MeC ₆ H ₅ , rt, 48 h	 I (>99) 76% ee	788
	Ph(1-Np)SiH ₂ (4 eq), [Rh(cod)Cl] ₂ (1 mol %), 41 , THF, -78°	 II (85) 86% ee	792
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod)Cl] ₂ (0.5 mol %), 37 (0.5 mol %), 0°	I (94) 60% ee	570
	Ph ₂ SiH ₂ (4 eq), [Rh(cod)Cl] ₂ (1 mol %), ligand II	II	792
	Ligand Solvent Temp	% ee	
41	none 0°	(54) 73	
41	none -40°	(79) 73	
41	THF 0°	(54) 73	
41	THF -78°	(86) 82	
40	THF -78°	(77) 51	
40	CH ₂ Cl ₂ -78°	(70) 48	
39	CCl ₄ 0°	(58) 14	
51	THF -78°	(45) 0	

Ph_2SiH_2 (1.5 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1 mol%),
ligand (1.1 mol%), THF, rt

Ligand	Time	% ee	
24	5 h	(89)	92
25	11 h	(88)	92
26	48 h	(78)	1
27	9 h	(85)	15



$\text{Ph}(1\text{-Np})\text{SiH}_2$ (1 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.3 mol%),
6 (0.4 mol%), THF, rt, 30 min



Ph_2SiH_2 (1 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.3 mol%),
ligand (0.4 mol%), THF, 30 min

Ligand	Temp	% ee		Conf.
40	rt	(92)	44	R
41	rt	(97)	73	R
41	10°	(94)	81	R
41	0°	(95)	82	R
42	rt	(65)	40	R
47	rt	(93)	52	R
49	rt	(55)	2	R
50	rt	(56)	4	S
45	rt	(97)	69	R
44	rt	(33)	17	S
46	rt	(99)	79	R
46	−40°	(99)	86	R
43	rt	(92)	26	R
53	rt	(85)	0	—
52	rt	(78)	3	R





TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	Ph_2SiH_2 (1.25 eq), 120 (0.5 %), MeC_6H_5 Temp -25° -10° 0° 20° 50°	 II % ee 35 25 17 2 4	791
	(EtO) ₃ SiH, 194 (10 mol%), Et_2O , 40°, 12 h	II (98) 53% ee	378
	PMHS (5 eq), CuCl, <i>t</i> -BuONa, 121 (0.0009 mol%), MeC_6H_5 , or THF, or MeC_6H_5 /THF, -78°	II (98) 92% ee	589
	Ph_2MeSiH (4 eq), CuCl (4 mol%), <i>t</i> -BuONa (4 mol%), 122 (3 mol%), MeC_6H_5 , -78°	II (90) 95% ee	589
	(HM_2Si) ₂ O (5 eq), CuCl (2 mol%), <i>t</i> -BuONa (2 mol %), 122 (1 mol%), MeC_6H_5 , -78°	II (98) 94% ee	589
	PMHS (10 eq), CuCl (3 mol %), <i>t</i> -BuONa (3 mol%), ligand (3 mol%), MeC_6H_5	II	589
	Ligand Time	% ee	
	121 5 h	94	
	122 1 h	90	
	123 6 h	95	
	124 <1 h	96	

Ligand	<div> <div> <div>OH</div> <div>Ph</div> </div> </div>		
	% Conv.	% ee	Conf.
182	95	75	S
183	97	74	S
186	98	72	S
184	95	70	S
185	98	73	S
181	98	56	S
180	97	48	S
179	95	30	S
154	98	18	S
140	98	24	S
158	99	70	S
143	95	52	S
155	98	62	S
156	97	63	S
157	98	62	S
141	95	47	R
146	98	88	R
142	98	83	R
144	97	83	R
145	15	58	R
135	99	75	R
153	98	8	R

PMHS (1.2 eq), Et₂Zn (2 mol%),
ligand (2 mol%), MeC₆H₅, rt, 24 h

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)						Refs.
		x		y		% ee		
	PMHS (1.1 eq), Et ₂ Zn (x mol%), (R,R)-ebpe (y mol%), vitride, (3%), MeC ₆ H ₅ , rt, 24 h	 I		(—)		20 20 76		594
	PMHS (1.1 eq), catalyst (2 mol%), ligand (2 mol%), MeC ₆ H ₅ , rt, 18 h	 I		2 2 74		2 2 74		594
	Catalyst	Ligand	Activator	% Conv.	% ee	Conf.		
	Me ₂ Zn	180	none	99	48	S		
	ZnH ₂	180	none	96	48	S		
	Ph ₂ ZnH•py	180	none	95	49	S		
	Et ₂ Zn	179	none	99	75	R		
	Et ₂ Zn•ebpe	179	none	99	75	R		
	Zn(dea) ₂	179	none	75	71	R		
	Zn(dea) ₂ •ebpe	179	none	70	71	R		
	Zn(dea) ₂	179	NaBH ₄ (2%)	100	45	R		
	Zn(dea) ₂	179	LiAlH ₄ (1%)	100	67	R		
	Zn(dea) ₂	179	vitride (3%)	100	72	R		
	Zn(dea) ₂	179	LiH (4%)	100	71	R		
	Cd(dea) ₂	179	none	100	62	R		
	Cd(dea) ₂	146	none	100	81	R		
	Co(daa) ₂	179	none	90	58	R		
	Cu(dea) ₂	179	none	0	—	—		
	Sn(2-EH) ₂	179	none	0	—	—		
	(MeHSiO) ₄ (3.75 eq), 197 (0.57 mol%), <i>n</i> -BuLi (1.14 mol%), THF, rt, 24 h	 II		(100) 99% ee				583
	PMHS (3.75 eq), 197 (0.57 mol%), <i>n</i> -BuLi (1.14 mol%), THF, rt, 24 h	II (100) 99% ee						583
	Ph ₂ SiH ₂ (1.5 eq), [Ir(cod)Cl] ₂ (0.25 mol%), 38 (0.5 mol%), Et ₂ O, 0°, 20 h	I (—) 96% ee						571



PMHS (1.2 eq), Et₂Zn (2 mol%),
ligand (2 mol%), MeC₆H₅, rt, 24 h

Ligand	% Conv.	% ee	Conf.
159	96	17	S
sparteine	60	19	R
160	98	55	S
173	67	6	R
174	100	8	S
175	60	13	R
176	9	1	S
43	88	10	S
187	100	32	S
177	10	5	R

II

Ph₂SiH₂ (1.1 eq), [Rh(cod)Cl]₂,
ligand (1 mol%), MeC₆H₅, 0°, 24 h

Ligand	% ee	Conf.
105	(97)	70 R
107	(86)	82 S
106	(92)	66 R
108	(89)	86 S
181	(89)	70 S




Ph₂SiH₂ (1.5 eq), [Rh(cod)₂]BF₄ (1 mol%),
31 (1.1 mol%), THF, -40°, 4 h

I (89) 94% ee

Ph₂SiH₂ (1.5 eq), [Rh(cod)₂]BF₄ (1 mol%),
31 (1.1 mol%), THF, -30°, 24 h

I (96) 80% ee

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
C ₈ 	PhSiH ₃ (1.1 eq), (<i>R</i>)- 195 -2 <i>n</i> -BuLi (x mol%), MeC ₆ H ₅ , rt	 1 % Conv. % ee 100 82 92 68 100 60 98 64 97 60 21 60	783																																																
	PhSiH ₃ (1.1 eq), (<i>R</i>)- 195 -2 <i>n</i> -BuLi (5 mol%), rt	 1	783																																																
	<table> <tr> <th>Solvent</th><th>Time</th><th>% Conv.</th><th>% ee</th></tr> <tr> <td>THF</td><td>1 h</td><td>87</td><td>6</td></tr> <tr> <td>THF</td><td>3 h</td><td>100</td><td>0</td></tr> <tr> <td>C₆H₅Me</td><td>1 h</td><td>44</td><td>59</td></tr> <tr> <td>C₆H₅Me</td><td>3 h</td><td>100</td><td>63</td></tr> <tr> <td>C₆H₆</td><td>1 h</td><td>78</td><td>36</td></tr> <tr> <td>C₆H₆</td><td>3 h</td><td>98</td><td>42</td></tr> <tr> <td><i>n</i>-C₆H₁₄</td><td>1 h</td><td>67</td><td>17</td></tr> <tr> <td><i>n</i>-C₆H₁₄</td><td>3 h</td><td>96</td><td>21</td></tr> <tr> <td>none</td><td>1 h</td><td>51</td><td>14</td></tr> <tr> <td>none</td><td>3 h</td><td>60</td><td>11</td></tr> <tr> <td>none</td><td>24 h</td><td>79</td><td>7</td></tr> </table>	Solvent	Time	% Conv.	% ee	THF	1 h	87	6	THF	3 h	100	0	C ₆ H ₅ Me	1 h	44	59	C ₆ H ₅ Me	3 h	100	63	C ₆ H ₆	1 h	78	36	C ₆ H ₆	3 h	98	42	<i>n</i> -C ₆ H ₁₄	1 h	67	17	<i>n</i> -C ₆ H ₁₄	3 h	96	21	none	1 h	51	14	none	3 h	60	11	none	24 h	79	7	1 (93) 74% ee	784
Solvent	Time	% Conv.	% ee																																																
THF	1 h	87	6																																																
THF	3 h	100	0																																																
C ₆ H ₅ Me	1 h	44	59																																																
C ₆ H ₅ Me	3 h	100	63																																																
C ₆ H ₆	1 h	78	36																																																
C ₆ H ₆	3 h	98	42																																																
<i>n</i> -C ₆ H ₁₄	1 h	67	17																																																
<i>n</i> -C ₆ H ₁₄	3 h	96	21																																																
none	1 h	51	14																																																
none	3 h	60	11																																																
none	24 h	79	7																																																
	PMHS (5 eq), CuF ₂ (<i>S</i>)-BINAP (4 mol%), MeC ₆ H ₅ , air, rt																																																		

PMHS (5 eq), CuF₂, (S)-BINAP (4 mol%),
MeC₆H₅, Ar, rt

I (100)

784

Me(EtO)₂SiH (1.5 eq), CuF₂,
(S)-BINAP (4 mol%), MeC₆H₅, air, rt

I (94)

784

PhSiH₃ (1,2-1.5 eq), [Cu] (x mol%),
(S)-BINAP, MeC₆H₅, atmosphere, rt

I

784

[Cu]	x	atm	Time	% ee
CuF ₂ , dppb	2	Ar	8 h	(90)
CuF ₂ , dppb	2	air	2 h	(99)
CuF ₂	4	Ar	16 h	(>99)
CuF ₂	1	air	2 h	(98)
CuF ₂	0.5	(—)	6 h	(94)
CuF(PPh ₃) ₃ •MeOH, dppb	4	Ar	2 h	(90)
CuF(PPh ₃) ₃ •MeOH	4	Ar	40 h	(91)
CuF(PPh ₃) ₃ •MeOH	2	air	1 h	(100)
CuI, Ph ₃ SiF ₂ N(Bu- <i>n</i>) ₄	1	Ar	24 h	(40)
[(Ph ₃ P)CuH] ₆	2	Ar	16 h	(95)



Silane (1.5 eq), **126** (1 mol%), THF, rt

I

576

Silane	% ee
PhSiH ₃	(—) 0
PhMeSiH ₂	(—) 78
Ph ₂ SiH ₂	(—) 88
Ph(1-Np)SiH ₂	(—) 95
Ph(<i>γ</i> -Bu)SiH ₂	(0) —
Et ₃ SiH	(0) —
PMHS	(0) —

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
<div>C₈ </div>	(EtO) ₃ SiH, THF, Ti(L) ₂ X ₂ , 2-3 d	<div> I</div>	793																																				
	<table><tr><th>L</th><th>X</th><th>% ee</th><th>Conf.</th></tr><tr><td>51</td><td>Cl</td><td>(60)</td><td>50 R</td></tr><tr><td>57</td><td>Cl</td><td>(20)</td><td>23 S</td></tr><tr><td>51</td><td>OPr-<i>i</i></td><td>(87)</td><td>18 S</td></tr><tr><td>59</td><td>OPr-<i>i</i></td><td>(85)</td><td>51 S</td></tr><tr><td>62</td><td>OPr-<i>i</i></td><td>(13)</td><td>65 S</td></tr><tr><td>59</td><td>F</td><td>(86)</td><td>61 S</td></tr><tr><td>60</td><td>F</td><td>(30)</td><td>56 S</td></tr><tr><td>61</td><td>F</td><td>(18)</td><td>51 S</td></tr></table>	L	X	% ee	Conf.	51	Cl	(60)	50 R	57	Cl	(20)	23 S	51	OPr- <i>i</i>	(87)	18 S	59	OPr- <i>i</i>	(85)	51 S	62	OPr- <i>i</i>	(13)	65 S	59	F	(86)	61 S	60	F	(30)	56 S	61	F	(18)	51 S		
L	X	% ee	Conf.																																				
51	Cl	(60)	50 R																																				
57	Cl	(20)	23 S																																				
51	OPr- <i>i</i>	(87)	18 S																																				
59	OPr- <i>i</i>	(85)	51 S																																				
62	OPr- <i>i</i>	(13)	65 S																																				
59	F	(86)	61 S																																				
60	F	(30)	56 S																																				
61	F	(18)	51 S																																				
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod)]SbF ₆ (1 mol%), ligand (1 mol%), THF, rt	<div>I</div>	576																																				
	<table><tr><th>Ligand</th><th>% ee</th><th>Conf.</th></tr><tr><td>127</td><td>(36)</td><td>62 S</td></tr><tr><td>128</td><td>(89)</td><td>51 S</td></tr><tr><td>129</td><td>(50)</td><td>20 R</td></tr><tr><td>130</td><td>(90)</td><td>86 R</td></tr></table>	Ligand	% ee	Conf.	127	(36)	62 S	128	(89)	51 S	129	(50)	20 R	130	(90)	86 R																							
Ligand	% ee	Conf.																																					
127	(36)	62 S																																					
128	(89)	51 S																																					
129	(50)	20 R																																					
130	(90)	86 R																																					



PMHS (1.2 eq), Et₂Zn (2 mol%),
ligand (2 mol%), MeC₆H₅, rt

Ligand	Time	% ee	Conf.
131	18 h	(98)	S
135	18 h	(99)	S
139	170 h	(56)	R
137	48 h	(11)	R
147	216 h	(30)	R
138	288 h	(66)	R
151	40 h	(56)	R
136	44 h	(78)	R
149	18 h	(>99)	S
150	72 h	(>99)	R



Ph₂SiH₂ (2 eq), (Ph₃P)RuCl₂ (1 mol%),
ligand (1 mol%), additive (1 mol%), Et₂O, 0°

Ligand	Additive	Time	% ee
37	AgOTf	24 h	(56)
37	Cu(OTf) ₂	24 h	(59)
37	—	24 h	(46)
35	AgOTf	5 h	(42)
35	Cu(OTf) ₂	36 h	(38)
36	AgOTf	24 h	(52)
41	AgOTf	70 h	(34)

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)






Ketone	Conditions	Product(s) and Yield(s) (%)			Refs.
C_8 	$[\text{Rh}(\text{cod})_2]\text{BF}_4$ (5 mol%), ligand (5 mol%)				789, 795
			Ligand	Solvent	
			Temp	Time	
			% ee	Conf.	
	Ph_2SiH_2 (1.5 eq), $[\text{Ir}(\text{cod})\text{Cl}]_2$ (2.5 mol%), ligand (5 mol%), THF				789
			Ligand	Temp	
			Time	% ee	
			Conf.		

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₈</div> <div></div>	<div>Ph₂SiH₂ (1.5 eq), [Rh(cod)Cl]₂ (0.5 mol %), ligand (1 or 2 mol %), THF, 0°, 20 h</div>	<div> II</div>	789
<div>Ligand</div>		<div>% ee</div>	
7		(51) 16	
13		(26) 40	
15		(30) 18	
14		(73) 8	
9		(81) 16	
10		(36) 12	
8		(25) 35	
12		(51) 0	
11		(39) 36	
32		(52) 33	
33		(44) 40	
3		(65) 31	
4		(73) 27	
5		(50) 32	
6		(73) 24	
191		(35) 5	
192		(83) 0	



Ph₂SiH₂ (1.5 eq), [Rh(cod)Cl]₂ (2.5 mol%),
ligand (5 mol%), MeOH

Ligand	Temp	Time	% ee	
29	0°	70 h	(46)	48
28	0°	40 h	(56)	10
30	0°	40 h	(72)	27

Ph₂SiH₂ (2 eq), [Rh(cod)Cl]₂ (1 mol%),
48 (x mol%), 0°

Solvent	x	% ee	
none	2.4	(64)	76
THF	2.4	(76)	85
Et ₂ O	2.4	(80)	91
MeC ₆ H ₅	2.4	(76)	93
MeC ₆ H ₅	4	(84)	94

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)				Refs.		
<div>C₈</div> <div></div>	Ph ₂ SiH ₂ (1.3 eq), catalyst (1 mol%), ligand, THF, rt, 24 h	<div></div> <div>II</div>				796		
			Catalyst	Ligand	% Conv.		% ee	Conf.
			[Rh(Cl)(cod)]•L	218	86		4.4	R
			[Rh(Cl)(cod)]•2L	219	90		0	—
			1/2[Rh(Cl)(cod)] ₂ •2L	218	93		11.2	R
			1/2[Rh(Cl)(cod)] ₂ •2L	219	94		4.4	R
			1/2[Rh(Cl)(cod)] ₂ •2L	217	93		6.8	R
			1/2[RhCl(C ₂ H ₄) ₂]•L	218	92		6.6	R
			[RhCl(C ₂ H ₄)•L] ₂	218	88		5.0	R
			1/2[RhCl(C ₂ H ₄) ₂]•2L	218	96		41.4	R
			1/2[RhCl(C ₂ H ₄) ₂]•2L	219	92		52.3	R
			1/2[RhCl(C ₂ H ₄) ₂]•2L	217	63		3.3	S
			1/2[RhCl(C ₂ H ₄) ₂]•3L	218	89		51.2	R
			1/2[RhCl(C ₂ H ₄) ₂]•3L	219	94		58.3	R
			RhCIL ₂	218	90		31.0	R
			[Rh(Cl)COL ₂]	218	78		7.5	R
			1/2[RhCl(C ₂ H ₄) ₂]•2L + C ₂ H ₄	218	92		33.1	R
			1/2[RhCl(C ₂ H ₄) ₂]•4L	218	83		27.6	R
1/2[RhCl(C ₂ H ₄) ₂]•5L	218	79	25.7	R				



Cl_3SiH (1.5 eq), CHO (0.1 eq),
 CH_2Cl_2 , 0° to rt, 24 h

II

R	Conf.	% ee	R:S
CONHPh	S	(90) 31	65:35
CONHPh	R	(93) 27	36:64
$\text{CONHC}_{10}\text{H}_7\text{-1}$	S	(78) 43	71:29
CONHCHPh_2	S	(69) 20	61:39
$\text{CONHC}_6\text{H}_{11}\text{-}n$	S	(82) 8	54:46
$\text{CONHBu-}t$	S	(80) 11	55:45
CO_2Ph	S	(53) 21	61:39
CO_2Me	S	(39) 14	57:43
$\text{CO}_2\text{Bu-}t$	S	(88) 11	55:45
CH_2OBn	S	(29) 13	56:44

379



Ph_3SiH_2 (1 eq), catalyst, ligand, C_6H_6 , rt, 16 h

II

Catalyst	Ligand	Rh:Ligand	% ee
$[\text{Rh}(\text{cod})\text{Cl}]_2$	TRISPHOS	1:2	(60) 0
$[\text{Rh}(\text{cod})\text{Cl}]_2$	(<i>S,S,S</i>)-TRISPHOS	1:2	(38) 81
$[\text{Rh}(\text{cod})\text{Cl}]_2$	(<i>S,S,S</i>)-TRISPHOS	1:3	(53) 75
(NBD)/Rh(acac)	(<i>S,S,S</i>)-TRISPHOS	1:1	(67) 58
(NBD)/RhClO ₄	(<i>S,S,S</i>)-TRISPHOS	1:1	(65) 81

797

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	R_3SiH (1 eq), Li-(<i>R</i>)-BINOL (5 mol%)	 I	592
	R_3Si Solvent Temp Time % ee		
	(MeO) $_3\text{Si}$ THF -78° ; 20° 6 h; 16 h (88) 0		
	(EtO) $_3\text{Si}$ Et $_2\text{O}$ 0°; 20° 6 h; 16 h (33) 31		
	(EtO) $_3\text{Si}$ Et $_2\text{O}$ /TMEDA 2:1 0° 24 h (50) 64		
	(EtO) $_3\text{Si}$ THF/TMEDA 2:1 0° 24 h (52) 33		
	(EtO) $_3\text{Si}$ Et $_2\text{O}$, TMEDA 0° 24h (46) 63		
	Ph_2SiH_2 (1.6 eq), complex (4.0 mol%), ligand (10 mol%), AgBF $_4$ (0.02 mol%), THF	I	580
	Complex Ligand Time % ee		
	99 89 3 h (94) 22		
	103 87 2 h (94) 31		
	99 87 2 h (88) 62		
	99 88 3 h (94) 84		
	102 87 7 h (87) 87		
	Ph_2SiH_2 (1.6 eq), complex (4.0 mol%), ligand (10 mol%), AgBF $_4$ (0.02 mol%), THF	I	580
	Complex Ligand Temp Time % ee		
	100 89 -5° 10 h (91) 91		
	101 88 0° 18 h (92) 83		
	103 92 10° 2 h (88) 54		
	104 93 20° 18 h (82) 19		
	102 91 20° 20 h (66) —		



Ph₂SiH₂ (1.25 eq), Rh[(NBD)Cl]₂ (0.5%),
ligand (0.5%), MeC₆H₅

Ligand	Temp	% ee
116	0°	52
117	10°	55
118	20°	54
119	20°	56
109	20°	55
113	20°	82

Ph₂SiH₂ (1.25 eq), Rh[(NBD)Cl]₂ (0.5%), **117**

Solvent	Rh[(NBD)Cl] ₂ : 117	Temp	% Conv.	% ee
MeC ₆ H ₅	1:1	-27°	57	17
MeC ₆ H ₅	1:1	0°	96	53
MeC ₆ H ₅	1:1	10°	96	55
MeC ₆ H ₅	1:1	20°	95	51
THF	1:1	-27°	39	15
THF	1:1	0°	88	52
THF	1:1	10°	79	49
C ₆ H ₆	1:1	0°	95	46
C ₆ H ₆	1:1	20°	86	49
MeC ₆ H ₅	1:1	10°	86	54
MeC ₆ H ₅	1:4	10°	97	56
MeC ₆ H ₅	1:2	10°	96	56

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																
C_8 	R_3SiH (1.6 eq), 87 (1.5 mol%), 99 (10 mol%), THF, -5° to 0°	 I	580																
	<table> <tr> <th>R_3Si</th><th>Temp</th><th>Time</th><th>% ee</th></tr> <tr> <td>Ph_2HSi</td><td>-5° to 0°</td><td>—</td><td>(—) 76-78</td></tr> <tr> <td>PhMeHSi</td><td>0°</td><td>26 h</td><td>(32) 14</td></tr> <tr> <td>$\text{Ph}(1\text{-Np})\text{HSi}$</td><td>$0^\circ$</td><td>4 d</td><td>(62) 62</td></tr> </table>	R_3Si	Temp	Time	% ee	Ph_2HSi	-5° to 0°	—	(—) 76-78	PhMeHSi	0°	26 h	(32) 14	$\text{Ph}(1\text{-Np})\text{HSi}$	0°	4 d	(62) 62		
R_3Si	Temp	Time	% ee																
Ph_2HSi	-5° to 0°	—	(—) 76-78																
PhMeHSi	0°	26 h	(32) 14																
$\text{Ph}(1\text{-Np})\text{HSi}$	0°	4 d	(62) 62																
	$(\text{EtO})_3\text{SiH}$, 194 (10 mol%)	I	378																
	<table> <tr> <th>Solvent</th><th>Temp</th><th>Time</th><th>% ee</th></tr> <tr> <td>Et_2O</td><td>50°</td><td>5 h</td><td>(>98) 55</td></tr> <tr> <td>MeC_6H_5</td><td>50°</td><td>5 h</td><td>(78) 48</td></tr> <tr> <td>none</td><td>40°</td><td>12 h</td><td>(>98) 54</td></tr> </table>	Solvent	Temp	Time	% ee	Et_2O	50°	5 h	(>98) 55	MeC_6H_5	50°	5 h	(78) 48	none	40°	12 h	(>98) 54		
Solvent	Temp	Time	% ee																
Et_2O	50°	5 h	(>98) 55																
MeC_6H_5	50°	5 h	(78) 48																
none	40°	12 h	(>98) 54																



(MeO)₃SiH (1 eq), catalyst




Catalyst	Solvent	Temp	Time	% ee	Conf.
Li-(<i>R</i>)-BINOL	Et ₂ O	0°	48 h	7	R
Li-(<i>R</i>)-BINOL	Et ₂ O/TMEDA 2:1 ^c	0°	12 h	48	S
(<i>R</i>)-BINOL phosphoric acid	THF	-22°	48 h	6	R
Li-(<i>R</i>)-BINOL	Et ₂ O/TMEDA 2:1 ^c	20°	24 h	64	S
Li-(<i>R</i>)-BINOL	Et ₂ O/TMEDA 30:1 ^c	20°	24 h	63	S
Al-BINOL complex	Et ₂ O or THF	20°	24 h	—	—
Li-(<i>R</i>)-2,2'-Me ₂ -BINOL	Et ₂ O/TMEDA 30:1	-20°	24 h	26	R
Li-(<i>R</i>)-methoxythio-BINOL	Et ₂ O/TMEDA 30:1	20°	24 h	37	R
Li-(<i>R</i>)-BINOL	Et ₂ O/TMEDA 30:1 ^d	0°	8 h	58	S
Li-(<i>R</i>)-BINOL	Et ₂ O/TMEDA 30:1 ^e	0°	8 h	59	S
Li-(<i>R</i>)-BINOL	Et ₂ O/TMEDA 30:1 ^f	0°	24 h	70	S
Li-(<i>R</i>)-BINOL	Et ₂ O/TMEDA 30:1 ^f	0°	24 h	70	S
Li-(<i>R</i>)-BINOL	Et ₂ O	0°	24 h	52	S
(<i>R</i>)-hydro-BINOL	Et ₂ O/TMEDA 30:1	0°	24 h	40	S
Li-(<i>R</i>)-BINOL	Et ₂ O/TMEDA 30:1 ^g	0°	24 h	66	S



Ph₂SiH₂ (1.7 eq), catalyst (x mol%),
ligand (y mol%)

Catalyst	x	Ligand	Temp	Time	% ee	Conf.
CuOBu- <i>t</i>	0.3	(-)-DIOP	0-20°	15 h	19.5	R
CuO ₂ CPh	0.3	(-)-DIOP	0-20°	23 h	18.7	R
CuO ₂ CPh	0.33	(-)-DIOP	0-20°	16 h	13.4	R
CuO ₂ CPh	0.48	(+)-NORPHOS	20°	95 h	38.8	R
CuO ₂ CPh	0.5	(+)-NORPHOS	20°	120 h	16.3	S
CuO ₂ CPh	0.24	(-)-BPFA	0-20°	18 h	28.9	R

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																
<div>C₈</div> <div></div>	R ₃ SiH, ligand, THF/TMEDA, 0°, 10 min	<div></div> <div>I</div>	593																
	<table><tr><th>R₃Si</th><th>Ligand</th></tr><tr><td>(EtO)₃Si</td><td>188</td></tr><tr><td>(MeO)₃Si</td><td>none</td></tr><tr><td>(EtO)₃Si</td><td>190</td></tr><tr><td>(EtO)₃Si</td><td>189</td></tr><tr><td>(MeO)₃Si</td><td>Li-histidine</td></tr><tr><td>(EtO)₃Si</td><td>Li₂-histidine</td></tr><tr><td>(EtO)₃Si</td><td>Li-phenylalanine</td></tr></table>	R ₃ Si	Ligand	(EtO) ₃ Si	188	(MeO) ₃ Si	none	(EtO) ₃ Si	190	(EtO) ₃ Si	189	(MeO) ₃ Si	Li-histidine	(EtO) ₃ Si	Li ₂ -histidine	(EtO) ₃ Si	Li-phenylalanine	<div>(55)</div> <div>(0)</div> <div>(26)</div> <div>(30)</div> <div>(26)</div> <div>(26)</div> <div>(25)</div>	
	R ₃ Si	Ligand																	
	(EtO) ₃ Si	188																	
	(MeO) ₃ Si	none																	
	(EtO) ₃ Si	190																	
	(EtO) ₃ Si	189																	
(MeO) ₃ Si	Li-histidine																		
(EtO) ₃ Si	Li ₂ -histidine																		
(EtO) ₃ Si	Li-phenylalanine																		
Ph ₂ SiH ₂ (1.7 eq), catalyst (x mol%), ligand (y mol%)	<div></div> <div>I</div>	798																	

Ph₂SiH₂ (160 mol%),
[RuCl₂(C₆H₆)₂ (0.5 mol%),
ligand (x mol%), AgOTf (2 mol%)

I

Ligand	x	Solvent	Time	% ee
125	8.8	none	48 h	(94) 38
125	4.4	CCl ₄	24 h	(0) —
125	4.4	MeC ₆ H ₅	24 h	(88) 23
125	4.4	dioxane	96 h	(45) 35
125	4.4	THF	24 h	(97) 54
(<i>R</i>)-BINAP	4.4	none	24 h	(95) 5 (R)
87	8.8	none	72 h	(16) 0

799

Ph₂SiH₂, **207** (1 mol%), rt

Solvent	% ee	Conf.
THF	(—) 63	R
MeCN	(8) 10	R
CCl ₄	(11) 12	S
DME	(92) 12	R
MeC ₆ H ₅	(24) 21	R



800



Ph₂SiH₂ (1.6 eq), **99** (10 mol%),
additive (x mol%), THF



Additive	x	Temp	Time	% ee
none	—	rt	—	(0) —
AgBF ₄	2.0	0°	3 h	(94) 95
AgPF ₆	2.0	−3°	5 h	(80) 87
AgOTf	1.0	−5°	27 h	(96) 89
BF ₃ •OEt ₂	1.5	0°	14 h	(90) 82
EtAlCl ₂	1.5	0°	18 h	(89) 67

580, 581

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)



Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₈</div> <div></div>	Ph ₂ SiH ₂ (1 eq), [Rh(cod)Cl] ₂ (0.5 mol%), 66 (2.5 mol%), 0–20°, 18 h	<div></div>	801
	Solvent	% ee	
	none	(60) 39.8	
	MeC ₆ H ₅	(66) 31.8	
	C ₆ H ₆	(60) 31.0	
	<i>n</i> -C ₅ H ₁₂	(45) 28.4	
	PE	(48) 24.2	
	Et ₂ O	(60) 34.0	
	THF	(51) 24.0	
	dioxane	(53) 25.2	
	CH ₂ Cl ₂	(71) 23.8	
	ClCH ₂ CH ₂ Cl	(72) 22.2	
	CHCl ₃	(76) 15.2	
CCl ₄	(93) 56.6		
MeCN	(63) 16.8		



Ph₂SiH₂ (1 eq), [Rh(cod)Cl]₂ (0.5 mol%),
ligand (2.5 mol%), MeC₆H₅, 0-20°, 18 h

Ligand		% ee	Conf.
64	(42)	25.5	R
65	(66)	31.8	S
66	(66)	34.4	R
67	(40)	20.2	S
69	(56)	23.0	R
68	(77)	37.4	R
70	(44)	32.8	R
71	(63)	39.8	R
72	(77)	70.1	R
73	(63)	26.5	S
74	(69)	33.8	S
75	(58)	39.6	R
76	(57)	3.6	R
77	(19)	4.3	S
78	(16)	4.2	R
79	(66)	34.7	S
80	(69)	33.8	R
81	(68)	53.6	S
82	(51)	8.7	R
83	(69)	24.3	R
84	(48)	1.7	R

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)




Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	Ph_3SiH_2 (1 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.5 mol%), ligand (2.5 mol%), CCl_4 , 0–20°, 18 h		801
	Ligand	% ee Conf.	
	64	(80) 40.7 R	
	66	(93) 56.6 S	
	67	(75) 52.6 S	
	69	(90) 53.2 R	
	68	(85) 62.2 R	
	70	(67) 69.8 R	
	71	(89) 71.6 R	
	72	(90) 83.4 R	
	73	(70) 66.6 S	
	74	(85) 50.0 S	
	75	(95) 62.4 R	
	76	(10) 42.9 R	
	77	(27) 5.6 S	
	78	(63) 9.0 R	
	79	(90) 49.6 S	
	80	(90) 50.8 R	
	81	(89) 65.6 S	
	82	(17) 10.4 R	
	83	(49) 46.5 R	
	84	(22) 7.6 R	



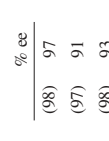

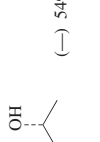
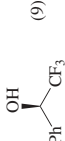





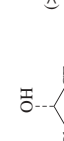

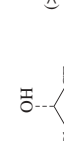


Ph₃SiH₂ (1.2 eq), [Rh(codCl)]₂ (0.5 mol%),
ligand or complex (x mol%), rt

Ligand or complex	x	Solvent	% ee
54	5	none	7 (36)
54	5	MeC ₆ H ₅	1 (61)
54	6	CCl ₄	55 (—)
58	5	MeC ₆ H ₅	5 (48)
58	2.5	CCl ₄	15 (—)
58	5	CCl ₄	84 (59)
55	5	MeC ₆ H ₅	9 (68)
55	5	CCl ₄	3 (21)
56	5	MeC ₆ H ₅	50 (72)
56	5	CCl ₄	33 (—)

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	PMHS (2 eq), Et ₂ Zn (2 mol%), ligand (2 mol%), MeC ₆ H ₅ , rt		788
	131 Ligand Time	% ee Conf.	
	18 h	(>99) 76 S	
	134 6 h	(94) 78 S	
	132 6 h	(14) 76 S	
	133 6 h	(68) 22 S	
	152 4 h	(15) 0 —	
	148 18 h	(>99) 88 R	
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂][BF ₄] (1.0 mol%), ligand (1.1 mol%), -40°		577
	Ligand Solvent Time	% ee Conf.	
	23 THF 24 h	(90) 85 S	
	24 THF 5 h	(89) 92 S	
	25 THF 11 h	(88) 92 S	
	26 THF 78 h	(78) 1 R	
	27 THF 9 h	(85) 15 S	
	25 DME 21 h	(96) 90 S	
	25 CH ₂ Cl ₂ 168 h	(81) 91 S	
	25 MeC ₆ H ₅ 4 h	(86) 90 S	
	25 THF 50 h	(95) 89 S	

<p>Ph₂SiH₂ (1.5 eq), catalyst (1 mol%), 95 (x mol%), AgX (2 mol%), THF</p>	<p>OSiPh₂H  I</p>	<p>+  II</p>	572																																						
<p>(EtO)₃SiH, 193 (10 mol%)</p>	<p>Catalyst x AgX Temp Time I % ee II</p> <tr> <td>Rh(cot)Cl</td><td>2</td><td>none</td><td>20°</td><td>2 h</td><td>(68)</td><td>41</td><td>(32)</td></tr> <tr> <td>Rh(cot)Cl</td><td>2</td><td>AgOTf</td><td>15°</td><td>3 h</td><td>(64)</td><td>43</td><td>(33)</td></tr> <tr> <td>Rh(cot)Cl</td><td>2</td><td>AgBF₄</td><td>15°</td><td>3 h</td><td>(57)</td><td>70</td><td>(39)</td></tr> <tr> <td>RhCl₃</td><td>2</td><td>none</td><td>rt</td><td>2 h</td><td>(86)</td><td>75</td><td>(14)</td></tr> <tr> <td>RhCl₃</td><td>4</td><td>AgBF₄</td><td>5°</td><td>2 h</td><td>(98)</td><td>90</td><td>(2)</td></tr>	Rh(cot)Cl	2	none	20°	2 h	(68)	41	(32)	Rh(cot)Cl	2	AgOTf	15°	3 h	(64)	43	(33)	Rh(cot)Cl	2	AgBF ₄	15°	3 h	(57)	70	(39)	RhCl ₃	2	none	rt	2 h	(86)	75	(14)	RhCl ₃	4	AgBF ₄	5°	2 h	(98)	90	(2)
Rh(cot)Cl	2	none	20°	2 h	(68)	41	(32)																																		
Rh(cot)Cl	2	AgOTf	15°	3 h	(64)	43	(33)																																		
Rh(cot)Cl	2	AgBF ₄	15°	3 h	(57)	70	(39)																																		
RhCl ₃	2	none	rt	2 h	(86)	75	(14)																																		
RhCl ₃	4	AgBF ₄	5°	2 h	(98)	90	(2)																																		
<p>  193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294</p>	<p> 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239</p>																															



PhSiH₃ (1.1 eq), (S)-**195**-2*n*-BuLi (5 mol%),
MeC₆H₅, 65°



Ar	Time	% Conv.	% ee
Ph	24 h	100	16
4-FC ₆ H ₄	1 h	38	12
4-ClC ₆ H ₄	1 h	18	13
4-O ₂ NC ₆ H ₄	1 h	9	2(S)
2-ClC ₆ H ₄	3 h	14	13
4-MeOC ₆ H ₄	1 h	100	23
4-MeC ₆ H ₄	1 h	100	6

783



1. **197** (4.5 eq), *n*-BuLi (9 eq), C₆H₆
2. PMHS (5 eq)
3. Add ketone, time
4. TBAF, THF



588

Ar	Time	% ee
Ph	0.9 d	(73) 97
2-BrC ₆ H ₄	8 d	(51) 94
2-ClC ₆ H ₄	2 d	(78) 90
2-MeOC ₆ H ₄	0.8 d	(77) 91
2-MeC ₆ H ₄	1 d	(88) 95
4-ClC ₆ H ₄	2 d	(85) 94
4-BrC ₆ H ₄	1 d	(75) 96
4-FC ₆ H ₄	1 d	(89) 97
4-CF ₃ C ₆ H ₄	8 d	(66) 65
4-MeC ₆ H ₄	0.9 d	(84) 96
4-MeOC ₆ H ₄	0.8 d	(62) 87

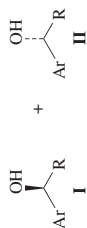
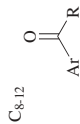
TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions			Product(s) and Yield(s) (%)	Refs.
	Silane	x	Time		
$\text{C}_{8,9} \quad \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{CH}_3 \end{array}$	R			$\begin{array}{c} \text{OH} \\ \\ \text{R}-\text{CH}-\text{CH}_3 \end{array}$	803
	Silane (2 eq), [Rh(C ₂ H ₄) ₂] ₂ (x mol%), (+)-DIOP (x mol%), C ₆ H ₆ , rt			Opt. Yield	
	Ph	Cl ₃ SiH	0.5 24 h	(0)	
	Ph	Et ₃ SiH	1.6 26 h	(47) 3.8%	
	Ph	Ph ₃ SiH	2 24 h	(15) 0%	
	Ph	(EtO) ₃ SiH	0.5 24 h	(60) 10%	
	Bn	Et ₃ SiH	1.6 20 h	(50) 1%	
	Bn	(EtO) ₃ SiH	1.6 48 h	(39) 5.3%	
	Ph	PMHS	2 24 h	(56) 3.6%	
	Bn	PMHS	2 48 h	(64) 0%	
$\text{C}_{8,10} \quad \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{R} \end{array}$	R ₃ SiH (2 eq), [Rh(C ₂ H ₄) ₂] ₂ (x mol%), (+)-DIOP (x mol%), C ₆ H ₆ , rt			$\begin{array}{c} \text{OH} \\ \\ \text{Ph}-\text{CH}-\text{R} \\ \text{I} \end{array}$	803
	R	R ₃ Si	x	Opt. Yield	
	Me	PhMeHSi	1.6	(48) 13%	
	Me	Ph ₂ HSi	2	(100) 28%	
	Me	Ph(1-Np)HSi	2	(100) 58%	
	<i>i</i> -Pr	PhMeHSi	2	(87) 20%	
	<i>i</i> -Pr	Ph ₂ HSi	2	(100) 35%	
	<i>i</i> -Pr	Ph(1-Np)HSi	2	(70) 24%	
	R ₃ SiH, [(−)-(S)-bmpp] ₂ RhCl, C ₆ H ₆ , 5–50°, 3–48 h			$\begin{array}{c} \text{OH} \\ \\ \text{Ph}-\text{CH}-\text{R} \end{array}$	
	R	R ₃ Si		Opt. Yield Conf.	
	Me	PhMe ₂ Si		(92) 44%	R
	Et	PhMe ₂ Si		(96) 50%	R
	<i>i</i> -Pr	PhMe ₂ Si		(95) 56%	R
	Et	Et ₂ HSi		(98) 17%	S
	<i>i</i> -Pr	Et ₂ HSi		(98) 23%	S

785, 786

R_3SiH (2 eq), $[Rh(C_2H_4)_2]_2$ resin (x mol%),
(+)-DIOP (2 mol%), C_6H_6 , rt



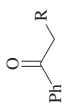
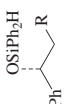
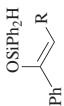
R	R_3Si	x
Me	PhMeHSi	4
Me	Ph ₂ HSi	2.8
Me	Ph(1-Np)HSi	2.8
Me	Ph(1-Np)HSi	5
<i>i</i> -Pr	PhMeHSi	4
<i>i</i> -Pr	Ph ₂ HSi	4



Ph_3SiH_2 (1.2 eq), C_6H_6 ,
 $[Rh(cod)Cl]_2$ (0.01 eq), ligand (0.1 eq),
0-20°, 10-15 h

Ar	R	Ligand	I + II	I:II
Ph	Me	109	(50)	70.5:29.5
Ph	Me	110	(28)	55:45
Ph	Me	111	(59)	22.5:77.5
Ph	Me	113	(40)	62.5:37.5
Ph	Me	114	(92)	19:81
Ph	Et	109	(60)	55:45
Ph	Et	110	(74)	23.5:76.5
1-Np	Me	109	(91)	9:91
1-Np	Me	110	(76)	10.5:89.5
1-Np	Me	113	(46)	49.5:50.5
1-Np	Me	114	(99)	8:92

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈₋₁₂ 	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1.0 mol%), ligand (1.1 mol%), -40°, DME	 <div> <div>% ee</div> <div> <div>(76)</div> <div>81</div> </div> <div> <div>(62)</div> <div>80</div> </div> <div> <div>(75)</div> <div>70</div> </div> <div> <div>(88)</div> <div>65</div> </div> <div> <div>(78)</div> <div>60</div> </div> <div> <div>(81)</div> <div>55</div> </div> <div> <div>(84)</div> <div>32</div> </div> <div> <div>(93)</div> <div>70</div> </div> <div> <div>(93)</div> <div>60</div> </div> <div> <div>(78)</div> <div>96</div> </div> <div> <div>(92)</div> <div>91</div> </div> </div>	577
C ₈₋₉ 	Ph ₂ SiH ₂ (1.2 eq), catalyst (1.0 mol%), THF, 16 h	<div>  <div>I</div> </div> <div> <div>+</div>  <div>II</div> </div>	805

R	Catalyst	Temp
H	203	rt
Me	203	rt
Et	203	rt
CH ₂ CH ₂ Cl	203	rt
H	204	rt
H	204	0°
Me	204	rt
Et	204	rt
CH ₂ CH ₂ Cl	204	rt
H	205	rt
Me	205	rt
Et	205	rt
CH ₂ CH ₂ Cl	205	rt
H	206	rt
Me	206	rt
Et	206	rt
CH ₂ CH ₂ Cl	206	rt

C₈₋₁₀



R₃SiH (x eq), [Rh(C₂H₄)₂]₂ (y mol%),
(+)-DIOP (x mol%), C₆H₆, rt

R ₃ Si	x	y
PhMeHSi	2	1.6
Ph ₂ HSi	2	2
Ph(1-Np)HSi	2	2
PhMeHSi	2	2
Ph ₂ HSi	2	2
Ph(1-Np)HSi	2	2

I + II	I	% ee
(91)	(89)	44
(82)	(79)	38
(81)	(80)	47
(90)	(84)	48
(98)	(95)	63
(88)	(81)	55
(95)	(93)	62
(96)	(92)	60
(95)	(89)	92
—	—	23
—	—	11
—	—	15
—	—	35
(96)	(92)	41
—	—	46
—	—	62
(88)	(77)	58



Opt. Yield
(48) 13%
(100) 28%
(100) 58%
(87) 20%
(100) 35%
(70) 24%

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions		Product(s) and Yield(s) (%)		Refs.
	Time	OH R ¹ —CH(R ²)	% Conv.	% ee	Conf.
C ₈ , ¹⁰ 	Ph ₂ SiH ₃ (1.2 eq), CuF ₂ (1%), (S)-BINAP (1%), MeC ₆ H ₅ , rt				
	Ph	Me	98	78	S
	Ph	Et	97	84	S
	Ph	<i>n</i> -Pr	100	92	S
	1-indanone		100	70	S
	Ph	CO ₂ Et	100	11	R
	4-ClC ₆ H ₄	Me	100	85	S
	3-ClC ₆ H ₄	Me	97	75	S
	2-ClC ₆ H ₄	Me	96	64	S
	4-CF ₃ C ₆ H ₄	Me	100	86	S
	3-CF ₃ C ₆ H ₄	Me	95	80	S
	4-FC ₆ H ₄	Me	100	82	S
	4-NCC ₆ H ₄	Me	95	86	—
	3, 5-(CF ₃) ₂ C ₆ H ₃	Me	100	85	—
	BnCH ₂	Me	100	20	R
	Ph ₂ SiH ₂ (1 eq), [Rh(cod)Cl] ₂ (0.5 mol%), 208 (2.5 mol%), 0-20°, 18 h				
	Ar	R	OH Ar—CH(R)		
	Ph	Me	(66)	31.8	
	Ph	<i>n</i> -Pr	(45)	18.0	
	2-MeC ₆ H ₄	Me	(28)	19.6	
	2-MeOC ₆ H ₄	Me	(67)	31.4	
	Ph	Me	(93)	56.6	
	Ph	<i>n</i> -Pr	(26)	42.6	
	2-MeC ₆ H ₄	Me	(59)	47.5	
	2-MeOC ₆ H ₄	Me	(78)	50.4	
	Solvent			% ee	
	MeC ₆ H ₅		(66)	31.8	
	MeC ₆ H ₅		(45)	18.0	
	MeC ₆ H ₅		(28)	19.6	
	MeC ₆ H ₅		(67)	31.4	
	CCl ₄		(93)	56.6	
	CCl ₄		(26)	42.6	
	CCl ₄		(59)	47.5	
	CCl ₄		(78)	50.4	

801



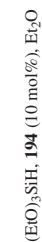
R ₃ Si	Li ₂ -2-Aminoethoxide	x	Temp	Time	% ee	
(MeO) ₃ Si	Li ₂ -alaninol	2.4	-78°	16 h	(62)	77
(MeO) ₃ Si	Li ₂ -alaninol	0.004	rt	3 h	(89)	44
(EtO) ₃ Si	Li ₂ -alaninol	0.004	rt	3 h	(75)	49
Me(OEt) ₂ Si	Li ₂ -alaninol	0.004	rt	3 h	(42)	48
(MeO) ₃ Si	Li ₂ -prolinol	0.004	rt	3 h	(89)	52
(MeO) ₃ Si	Li ₂ -prolinol	0.004	-78°	16 h	(100)	49
(MeO) ₃ Si	Li ₂ -valinol	0.004	rt	3 h	(99)	49
(MeO) ₃ Si	Li ₂ -alaninol	2.4	rt	3 h	(44)	72
(MeO) ₃ Si	Li ₂ -alaninol	0.004	rt	3 h	(88)	32
(MeO) ₃ Si	Li ₂ -prolinol	0.004	rt	3 h	(85)	45
(MeO) ₃ Si	Li ₂ -alaninol	2.4	rt	3 h	(52)	12
(MeO) ₃ Si	Li ₂ -alaninol	2.4	rt	3 h	(55)	17
(MeO) ₃ Si	Li ₂ -alaninol	2.4	rt	16 h	(12)	84

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₈₋₁₁</div> <div> </div>	<div>(MeO)₃SiH (1.2 eq), Li₂-diolate (2.4 eq), THF, 0°, 15–20 h</div> <div>Li₂-Diolate</div>	<div> </div> <div>% ee</div>	92
R	170	(41)	22
Me	171	(66)	40
Me	172	(78)	44
Et	170	(52)	36
Et	171	(70)	53
Et	172	(66)	54
<i>n</i> -Pr	170	(67)	36
<i>n</i> -Pr	171	(67)	66
<i>n</i> -Pr	172	(71)	62
<i>i</i> -Pr	170	(48)	44
<i>i</i> -Pr	171	(63)	69
<i>i</i> -Pr	172	(55)	69
<i>n</i> -Bu	170	(51)	44
<i>n</i> -Bu	171	(59)	63
<i>n</i> -Bu	172	(64)	55
<div>C₈₋₁₂</div> <div> </div>	<div>Ph₂SiH₂ (1.5 eq), [Rh(cod)₂]BF₄ (1.0 mol%), 25 (1.1 mol%), –40°, THF</div> <div>Time</div>	<div> </div> <div>% ee</div>	577
R ¹	90	(90)	91
R ²	5 h	(88)	86
Me	7 h	(87)	85
4-MeC ₆ H ₄	6 h	(79)	84
4-MeOC ₆ H ₄	6 h	(88)	79
3-MeOC ₆ H ₄	13 h	(84)	97
2-MeOC ₆ H ₄	11 h	(76)	82
4-ClC ₆ H ₄	9 h	(73)	62
Me	48 h		
Fc			
1-C ₁₀ H ₇			
Et			



Ar	Catalyst	Time	% ee	Conf.
Ph	199	2 h	12	S
Ph	201	2 h	5	R
Ph	200	2 h	7	S
Ph	196	13 h	14	S
4-MeC ₆ H ₄	196	58 h	0	—
4-MeOC ₆ H ₄	196	80 h	5	S
4-BrC ₆ H ₄	196	2 h	32	S
4-CF ₃ C ₆ H ₄	196	0.7 h	2	S
2-C ₁₀ H ₇	199	6 h	13	S
2-C ₁₀ H ₇	201	6 h	6	R
2-C ₁₀ H ₇	200	6 h	20	S
2-C ₁₀ H ₇	196	24 h	40	S



R	Temp	Time
Ph	50°	5 h
4-MeOC ₆ H ₄	50°	5 h
4-ClC ₆ H ₄	50°	5 h
4-O ₂ NC ₆ H ₄	50°	5 h
3-O ₂ NC ₆ H ₄	50°	5 h
<i>n</i> -C ₆ H ₁₃	40°	12 h
C ₆ H ₁₁	40°	12 h
<i>n</i> -BuC≡C	50°	5 h
(<i>E</i>)- <i>n</i> -C ₃ H ₁₁ CH=CH	40°	12 h
1-C ₁₀ H ₇	40°	12 h



TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{8,12}$ $ \begin{array}{c} O \\ \parallel \\ R-C \end{array} $	Ph_3SiH_2 (160 mol%), $[RuCl_2(C_6H_6)]_2$ (0.5 mol%), 125 (2.2 mol%), AgOTf (2 mol %), THF, rt	$ \begin{array}{c} OH \\ \\ R-CH \end{array} $	799
R	Time	% ee	
Ph	24 h	(97)	54
2-BrC ₆ H ₄	72 h	(87)	57
3-BrC ₆ H ₄	72 h	(93)	62
4-BrC ₆ H ₄	48 h	(93)	55
1-C ₁₀ H ₇	30 h	(85)	48
2-C ₁₀ H ₇	24 h	(98)	66
$ \begin{array}{c} O \\ \parallel \\ R^1-C-R^2 \end{array} $	Ph_3SiH_2 (2 eq), $[Rh(cod)Cl]_2$ (1 mol%), 48 (4 mol%), MeC ₆ H ₅ , rt	$ \begin{array}{c} OH \\ \\ R^1-CH-R^2 \\ \textbf{I} \end{array} $	585
R^1		% ee	
Ph		(84)	94
Ph		(91)	91
(<i>E</i>)-PhCH=CH		(83)	22
<i>c</i> -C ₆ H ₁₁		(85)	87
<i>n</i> -C ₆ H ₁₃		(90)	52
1-C ₁₀ H ₇		(90)	92
R^2			
Me			
Et			
R^1			
Ph			
4-MeOC ₆ H ₄			
4-CF ₃ C ₆ H ₄			
2,4-Me ₂ C ₆ H ₃			
2,4,6-Me ₃ C ₆ H ₂			
Ph			
1-C ₁₀ H ₇			
R^2		% ee	
Me		(94)	98
Me		(97)	97
Me		(88)	96
Me		(97)	95
Me		(99)	98
Et		(96)	98
Me		(97)	99
Ph_3SiH_2 , $[Rh(cod)Cl]_2$ (2.5 mol%), (–)- 34 , THF, rt		$ \begin{array}{c} OH \\ \\ R^1-CH-R^2 \end{array} $	586



o-ToI₂SiH₂, [Rh(cod)Cl]₂ (1.0 mol%),
34, THF, 0°



% ee	
(81)	72
(91)	94
(98)	82
(92)	96

586

C₈-13



(MeO)₃SiH (1 eq), Li₂-histidine (10 mol%),
 THF/TMEDA, 0°, 24 h







% ee	
(70)	26
(85)	26
(86)	30
(80)	40
(89)	70
(90)	—
(90)	—
(95)	30
(82)	5
(78)	5

593

R ¹	R ²
Ph	Me
Ph	Me
4-CF ₃ C ₆ H ₄	Me
4-MeC ₆ H ₄	Me
4-MeOC ₆ H ₄	Me
Bn	Me
Ph	Ph
4-CF ₃ C ₆ H ₄	Ph
4-MeC ₆ H ₄	Ph
4-MeOC ₆ H ₄	Ph

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

	Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																																												
C ₈₋₁₃		R ₃ SiH, [(+)-(R)-bmpp] ₂ RhCl, C ₆ H ₆ , 5-50°, 3-48 h		785																																												
		<table><tr><th>R</th><th>R₃Si</th><th>Opt. Yield</th><th>Conf.</th></tr><tr><td>Me</td><td>Et₂HSi</td><td>(97)</td><td>1%</td><td>R</td></tr><tr><td>Et</td><td>Ph₂SiH₂</td><td>(98)</td><td>42%</td><td>R</td></tr><tr><td><i>i</i>-Pr</td><td>Ph₂HSi</td><td>(96)</td><td>16%</td><td>S</td></tr><tr><td><i>i</i>-Pr</td><td>PhMeHSi</td><td>(93)</td><td>12%</td><td>S</td></tr><tr><td><i>i</i>-Bu</td><td>EtMe₂Si</td><td>(97)</td><td>56%</td><td>R</td></tr><tr><td><i>i</i>-Bu</td><td>PhMe₂Si</td><td>(92)</td><td>54%</td><td>S</td></tr><tr><td><i>c</i>-C₆H₁₁</td><td>PhMe₂Si</td><td>(90)</td><td>58%</td><td>S</td></tr><tr><td><i>c</i>-C₆H₁₁</td><td>Et₂HSi</td><td>(95)</td><td>19%</td><td>R</td></tr></table>	R	R ₃ Si	Opt. Yield	Conf.	Me	Et ₂ HSi	(97)	1%	R	Et	Ph ₂ SiH ₂	(98)	42%	R	<i>i</i> -Pr	Ph ₂ HSi	(96)	16%	S	<i>i</i> -Pr	PhMeHSi	(93)	12%	S	<i>i</i> -Bu	EtMe ₂ Si	(97)	56%	R	<i>i</i> -Bu	PhMe ₂ Si	(92)	54%	S	<i>c</i> -C ₆ H ₁₁	PhMe ₂ Si	(90)	58%	S	<i>c</i> -C ₆ H ₁₁	Et ₂ HSi	(95)	19%	R		
		R	R ₃ Si	Opt. Yield	Conf.																																											
		Me	Et ₂ HSi	(97)	1%	R																																										
		Et	Ph ₂ SiH ₂	(98)	42%	R																																										
		<i>i</i> -Pr	Ph ₂ HSi	(96)	16%	S																																										
		<i>i</i> -Pr	PhMeHSi	(93)	12%	S																																										
		<i>i</i> -Bu	EtMe ₂ Si	(97)	56%	R																																										
		<i>i</i> -Bu	PhMe ₂ Si	(92)	54%	S																																										
		<i>c</i> -C ₆ H ₁₁	PhMe ₂ Si	(90)	58%	S																																										
<i>c</i> -C ₆ H ₁₁	Et ₂ HSi	(95)	19%	R																																												
C ₈₋₁₄		Ph(1-Np)SiH ₂ (1.5 eq), 126 (1 mol%), THF, -20°		576																																												
		<table><tr><th>Ar</th><th>R</th><th>ee (%)</th></tr><tr><td>Ph</td><td>Me</td><td>(80) 95</td></tr><tr><td>2-MeC₆H₄</td><td>Me</td><td>(98) 95</td></tr><tr><td>4-MeC₆H₄</td><td>Me</td><td>(90) 92</td></tr><tr><td>2-MeOC₆H₄</td><td>Me</td><td>(90) 95</td></tr><tr><td>4-MeOC₆H₄</td><td>Me</td><td>(56) 88</td></tr><tr><td>2-ClC₆H₄</td><td>Me</td><td>(90) 98</td></tr><tr><td>4-ClC₆H₄</td><td>Me</td><td>(95) 85</td></tr><tr><td>1-C₁₀H₇</td><td>Me</td><td>(99) 98</td></tr><tr><td>2-C₁₀H₇</td><td>Me</td><td>(99) 95</td></tr><tr><td>Ph</td><td>Et</td><td>(95) 94</td></tr><tr><td>Ph</td><td><i>i</i>-Bu</td><td>(95) 94</td></tr><tr><td>Ph</td><td>Bn</td><td>(75) 94</td></tr></table>	Ar	R	ee (%)	Ph	Me	(80) 95	2-MeC ₆ H ₄	Me	(98) 95	4-MeC ₆ H ₄	Me	(90) 92	2-MeOC ₆ H ₄	Me	(90) 95	4-MeOC ₆ H ₄	Me	(56) 88	2-ClC ₆ H ₄	Me	(90) 98	4-ClC ₆ H ₄	Me	(95) 85	1-C ₁₀ H ₇	Me	(99) 98	2-C ₁₀ H ₇	Me	(99) 95	Ph	Et	(95) 94	Ph	<i>i</i> -Bu	(95) 94	Ph	Bn	(75) 94							
		Ar	R	ee (%)																																												
		Ph	Me	(80) 95																																												
		2-MeC ₆ H ₄	Me	(98) 95																																												
		4-MeC ₆ H ₄	Me	(90) 92																																												
		2-MeOC ₆ H ₄	Me	(90) 95																																												
		4-MeOC ₆ H ₄	Me	(56) 88																																												
		2-ClC ₆ H ₄	Me	(90) 98																																												
		4-ClC ₆ H ₄	Me	(95) 85																																												
1-C ₁₀ H ₇	Me	(99) 98																																														
2-C ₁₀ H ₇	Me	(99) 95																																														
Ph	Et	(95) 94																																														
Ph	<i>i</i> -Bu	(95) 94																																														
Ph	Bn	(75) 94																																														

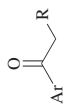


(MeO)₃SiH (1 eq), Et₂O:TMEDA (30:1),
Li-(*R*)-BINOL (5 mol%), 0°

R ¹	R ²	Time	% ee	Conf.
Ph	Me	6 h	61	S
2-BrC ₆ H ₄	Me	24 h	(91) 66	S
BnCH ₂	Me	24 h	(74) 46	R
Ph	MeO ₂ C(CH ₂) ₂	24 h	(63) 65	S
Ph	<i>i</i> -Bu	24 h	(60) 81	S
2,4,6-Me ₃ C ₆ H ₂	Me	24 h	(57) 90	R
1-C ₁₀ H ₇	Me	24 h	(67) 77	S
4-MeC ₆ H ₄	Ph	24 h	(74) 0	—
4-CF ₃ C ₆ H ₄	Ph	24 h	(90) 0	—

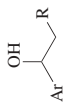


572



(EtO)₃SiH, THF, **198**, 96 h

Ar	R	% ee	Conf.
4-BrC ₆ H ₄	H	(61) 83	R
4-BrC ₆ H ₄	Cl	(50) 65	R
4-EtC ₆ H ₄	H	(60) 84	R
4-BrC ₆ H ₄	Me	(53) 80	R
4-BrC ₆ H ₄	OMe	(50) 78	R
4- <i>i</i> -PrC ₆ H ₄	H	(61) 85	S
4-BrC ₆ H ₄	Ph	(58) 75	S



793

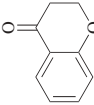
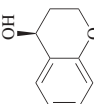
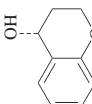
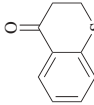
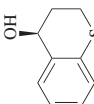
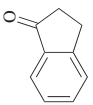
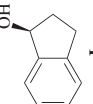
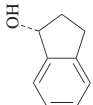
TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

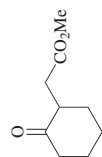
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.																														
C_{8-15} 	(MeO) ₃ SiH (1.2 eq), 178 , THF, 0°, 20 h	 <div><div><div>OH</div><div>Ar</div><div>R</div></div><div>+</div><div><div>OH</div><div>Ar</div><div>R</div></div></div> <div><div>I</div><div>II</div></div>	807																														
		<table><tr><th>I + II</th><th>% ee</th><th>Conf.</th></tr><tr><td>(93)</td><td>28</td><td>S</td></tr><tr><td>(95)</td><td>42</td><td>S</td></tr><tr><td>(59)</td><td>12</td><td>S</td></tr><tr><td>(93)</td><td>65</td><td>S</td></tr><tr><td>(>95)</td><td>82</td><td>S</td></tr><tr><td>(>95)</td><td>20</td><td>S</td></tr><tr><td>(59)</td><td>22</td><td>S</td></tr><tr><td>(50)</td><td>20</td><td>S</td></tr><tr><td>(0)</td><td>—</td><td>—</td></tr></table>	I + II	% ee	Conf.	(93)	28	S	(95)	42	S	(59)	12	S	(93)	65	S	(>95)	82	S	(>95)	20	S	(59)	22	S	(50)	20	S	(0)	—	—	
I + II	% ee	Conf.																															
(93)	28	S																															
(95)	42	S																															
(59)	12	S																															
(93)	65	S																															
(>95)	82	S																															
(>95)	20	S																															
(59)	22	S																															
(50)	20	S																															
(0)	—	—																															
C_9 	PMHS (1.1 eq), Et ₂ Zn (20 mol%), (<i>R,R</i>)-ebpe (20 mol%), vitride (3%), MeC ₆ H ₅ , rt, 24 h	 <div><div><div>OH</div><div>Ar</div><div>R</div></div><div>I</div></div> (—) 71% ee	594																														
	PMHS (1.1 eq), Et ₂ Zn (2 mol%), (<i>R,R</i>)-ebpe (20 mol%), vitride (3%), MeC ₆ H ₅ , rt, 24 h	 <div><div><div>OH</div><div>Ar</div><div>R</div></div><div>I</div></div> (—) 66% ee	594																														
	PMHS (5 eq), CuCl, <i>t</i> -BuONa, 121 (0.005 mol%), MeC ₆ H ₅ , or THF, or MeC ₆ H ₅ /THF, -78°	 <div><div><div>OH</div><div>Ar</div><div>R</div></div><div>I</div></div> (85) 95% ee	589																														
	PMHS (1.1 eq), Et ₂ Zn (2 mol%), (<i>R,R</i>)-ebpe (20 mol%), vitride (3%), MeC ₆ H ₅ , rt, 24 h	 <div><div><div>OH</div><div>Ar</div><div>R</div></div><div>I</div></div> (—)	<table><tr><th>Ar</th><th>% ee</th></tr><tr><td>3-MeOC₆H₄</td><td>73</td></tr><tr><td>4-MeOC₆H₄</td><td>72</td></tr></table>	Ar	% ee	3-MeOC ₆ H ₄	73	4-MeOC ₆ H ₄	72	594																							
Ar	% ee																																
3-MeOC ₆ H ₄	73																																
4-MeOC ₆ H ₄	72																																



PMHS (1.1 eq), Et ₂ Zn (2 mol%), (<i>R,R</i>)-ebpe (20 mol%), vitride (3%), MeC ₆ H ₅ , rt, 24 h	 I	(—) 81% ee	594
PMHS, Sn(OTf) ₂ (10 mol%), 93 (10 mol%), MeOH, rt, 12-14 h	 II	(98) 48% ee	385
1. 197 (4.5 eq), <i>n</i> -BuLi (9 eq), C ₆ H ₆ 2. PMHS (5 eq) 3. Add ketone, 1 d 4. TBAF, THF	II (96) 95% ee		588
(3-FC ₆ H ₄) ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1 mol%), 1 (1.1 mol%), THF, -40°, 24 h	I (99) 88% ee		578
Ph ₂ SiH ₂ (1.25 eq), Rh[(NBD)Cl] ₂ (0.5%), ligand (0.5%), MeC ₆ H ₅	I (—)		791
	Ligand	Temp	% ee
	116	0°	37
	117	20°	35
	118	0°	45
	119	20°	46
	109	20°	56
	113	20°	66

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ph_2SiH_2 (1.1 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.5 mol%), 108 (1.2 mol%), 0° , 24 h	 I (90) 95% ee (86) 87% ee	575
	$\text{Ph}(\text{1-Np})\text{SiH}_2$ (1.5 eq), 126 (1 mol%), THF, -20°	I (90) 95% ee	576
	PMHS, $\text{Sn}(\text{OTf})_2$ (10 mol%), 93 (10 mol%), MeOH, rt	 (77) 12% ee	385
	$\text{Ph}(\text{1-Np})\text{SiH}_2$ (1.5 eq), 126 (1 mol%), THF, -20°	 (90) 92% ee	576
	$\text{Ph}(\text{1-Np})\text{SiH}_2$ (1.5 eq), 126 (1 mol%), THF, -20°	 I (87) 87% ee (90) 85% ee	576
	Ph_2SiH_2 (1.5 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1.0 mol%), 25 (1.1 mol%), -40° , THF, 3 h	I (87) 87% ee	577
	1. 197 (4.5 eq), <i>n</i> -BuLi (9 eq), C_6H_6 2. PMHS (5 eq) 3. Add ketone, 1.6 d 4. TBAF, THF	I (68) 92% ee	588
	Ph_2SiH_2 (1 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.3 mol%), 41 (0.4 mol%), THF, rt, 30 min	 (85) 50% ee	787



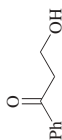
Ph₂SiH₂ (1.3 eq), RhCl₃ (1 mol%),
92 (5 mol%), AgBF₄ (2 mol%), THF, 0°, 1 d

390



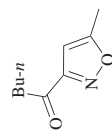
PMHS (1.2 eq), R₂Zn (2 mol%),
131 (2 mol%), MeC₆H₅, rt, 6 h

788



1. PhSiH₃ (0.1 eq), **198** (2 mol%),
 pyrrolidine, MeOH, THF, 60°
 2. PMHS, ketone, MeOH (3·7 eq), 15°

587



PMHS (4 eq), **124** (0.05 mol%), CuCl (1 mol%),
 NaOBu-*t* (1 mol%), THF/MeC₆H₅, -50°, 10 h

590

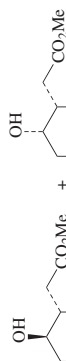
C_{9,10}



1. PhSiH₃ (0.1 eq), **198** (0.2 eq), MeOH, 60°
 2. PMHS (6-10 eq), additive (x eq), rt

587

Ar	R
4-MeC ₆ H ₄	Me
4-MeC ₆ H ₄	Me
Ph	<i>i</i> -Pr
Ph	<i>i</i> -Pr
Ph	<i>i</i> -Pr
Ph	<i>i</i> -Pr
Ph	<i>i</i> -Pr
Ph	<i>i</i> -Pr



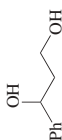
I + **II** (76), **I:II** = 54:46
 1S,2S 92% ee

390

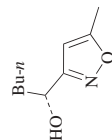


1S,2R 95% ee

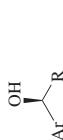
R	Time	% ee
Et	6 h	28
<i>i</i> -Pr	6 h	33
Ph	4 h	48



(50) 96% ee^b



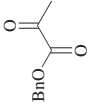
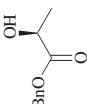
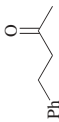
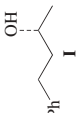


(68) 83% ee



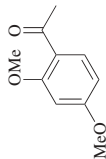
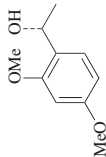
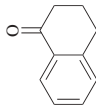
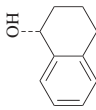
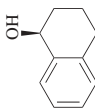
Ar	R	% ee
Ph	Me	97
Ph	Me	97
Ph	Me	97
Ph	Me	97
Ph	Me	97
Ph	Me	97
Ph	Me	97
Ph	Me	97

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-13} 	1. PhSiH_3 (0.1 eq), 198 (x mol%), pyrrolidine, MeOH, THF, 60° 2. PMHS, ketone, MeOH (3-7 eq), 15°		587
	Ar	% ee	
4-MeC ₆ H ₄	x	Time	(87) 98
Me	1	5 h	(86) 98
Ph	1	12 h	(86) 98
<i>i</i> -Pr	0.5	13 h	(86) 99
Ph	1	8 h	(80) >98
<i>c</i> -C ₆ H ₁₁	1	10 h	
Me ₂ C=CH(CH ₂) ₂	1		
C_{10} 	Ph(1-Np)SiH ₂ (1.5 eq), 126 (1 mol%), THF, -20°		576
		(92) 46% ee	
	(MeO) ₃ SiH (1 eq), Li ₂ -histidine (10 mol%), THF/TMEDA, 0°, 24 h		593
		(91) 28% ee	
	1. 197 (4.5 eq), <i>n</i> -BuLi (9 eq), C ₆ H ₆ 2. PMHS (5 eq) 3. Add ketone, 0.8 d 4. TBAF, THF	I (88) 12% ee	588

	Ph_2SiH_2 (1.5 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1 mol%), 1 (1.1 mol%), THF, -50° , 48 h		(94) 81% ee	578															
	$\text{Ph}(1\text{-Np})\text{SiH}_2$ (4 eq), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (1 mol%), 92 , THF, -78°		(70) 59% ee	792															
	PMHS (5 eq), CuCl , <i>t</i> -BuONa, 121 (0.005 mol%), MeC_6H_5 , or THF, or $\text{MeC}_6\text{H}_5/\text{THF}$, -78°	1 (87) 97% ee		589															
	$(3\text{-FC}_6\text{H}_4)_2\text{SiH}_2$ (1.5 eq), $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (1 mol%), 1 (1.1 mol%), THF, -40° , 24 h		<table><tr><th>R</th><th>% ee</th></tr><tr><td>H</td><td>(93) 89</td></tr><tr><td>Cl</td><td>(99) 88^b</td></tr></table>	R	% ee	H	(93) 89	Cl	(99) 88 ^b	578									
R	% ee																		
H	(93) 89																		
Cl	(99) 88 ^b																		
	1. 197 (4.5 eq), <i>n</i> -BuLi (9 eq), C_6H_6 2. PMHS (5 eq) 3. Add ketone, 4.5 d 4. TBAF, THF		(79) 92% ee	588															
	Ph_2SiH_2 (1.25 eq), $\text{Rh}(\text{NBD})\text{Cl}_2$ (0.5%), ligand (0.5%), MeC_6H_5		(—)	791															
	<table><tr><th>Ligand</th><th>Temp</th><th>% ee</th></tr><tr><td>116</td><td>0°</td><td>67</td></tr><tr><td>117</td><td>0°</td><td>65</td></tr><tr><td>118</td><td>0°</td><td>66</td></tr><tr><td>119</td><td>20°</td><td>66</td></tr></table>	Ligand	Temp	% ee	116	0°	67	117	0°	65	118	0°	66	119	20°	66			
Ligand	Temp	% ee																	
116	0°	67																	
117	0°	65																	
118	0°	66																	
119	20°	66																	
	PMHS, $\text{Sn}(\text{OTf})_2$ (10 mol%), 93 (10 mol%), MeOH, rt, 12–14 h	1 (96) 44% ee		385															

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.															
C ₁₀ 	PMHS (5 eq), CuCl, <i>t</i> -BuONa, 121 (0.005 mol%), MeC ₆ H ₅ , or THF, or MeC ₆ H ₅ /THF, -78°	 (89) 94% ee	589															
	PMHS (5 eq), CuCl, <i>t</i> -BuONa, 121 (0.005 mol%), MeC ₆ H ₅ , or THF, or MeC ₆ H ₅ /THF, -78°	 I (92) 99% ee	589															
	Ph(1-Np)SiH ₂ (4 eq), [Rh(cod)Cl] ₂ (1 mol%), 92 , THF, -78°	I (70) 48% ee	792															
	PMHS, Sn(OTf) ₂ (10 mol%), 93 (10 mol%), MeOH, rt	I (80) 43% ee	385															
	Ph ₂ SiH ₂ (2 eq), [Rh(cod)Cl] ₂ (1 mol%), (-)- 44 (4 mol%), MeC ₆ H ₅ , rt	 II (97) 92% ee	585															
	(MeO) ₃ SiH (1 eq), Et ₂ OTMEDA (30:1), Li-(<i>R</i>)-BINOL (10 mol%), 0°, 24 h	I (39) 93% ee	592															
	Ph ₂ SiH ₂ (2 eq), [Rh(cod)Cl] ₂ (1 mol%), 44 (x mol%), solvent, 0°	II	585															
<table><tr><th>Solvent</th><th>x</th><th>% ee</th></tr><tr><td>THF</td><td>2.4</td><td>(68) 43</td></tr><tr><td>MeC₆H₅</td><td>2.4</td><td>(76) 59</td></tr><tr><td>MeC₆H₅</td><td>4</td><td>(89) 89</td></tr><tr><td>MeC₆H₅</td><td>10</td><td>(84) 89</td></tr></table>			Solvent	x	% ee	THF	2.4	(68) 43	MeC ₆ H ₅	2.4	(76) 59	MeC ₆ H ₅	4	(89) 89	MeC ₆ H ₅	10	(84) 89	
Solvent	x	% ee																
THF	2.4	(68) 43																
MeC ₆ H ₅	2.4	(76) 59																
MeC ₆ H ₅	4	(89) 89																
MeC ₆ H ₅	10	(84) 89																


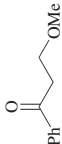
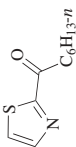
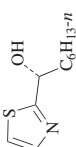
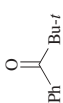


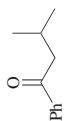
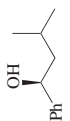
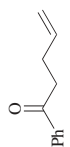

Ph ₂ SiH ₂ (1.6 eq), 92 (4.0 mol%), AgBF ₄ (0.02 mol%), THF, 0°, 2 h	I (92) 99% ee	580
Ph ₂ SiH ₂ (1.5 eq), [Rh(cod)Cl] ₂ (0.25 mol%), 38 (0.5 mol%), Et ₃ O, rt	II (95) 57% ee	571
Ph ₂ SiH ₂ (1.1 eq), [Rh(cod)Cl] ₂ (0.5 mol%), 106 (1.2 mol%), 0°, 42 h	I (70) 80% ee	575
Ph(1-Np)SiH ₂ (1.5 eq), 126 (1 mol%), THF, -20°	I (90) 91% ee	576
Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1.0 mol%), 25 (1.1 mol%), -40°, THF, 4 h	I (83) 84% ee	577
1. 197 (4.5 eq), <i>n</i> -BuLi (9 eq), C ₆ H ₆ 2. PMHS (5 eq) 3. Add ketone, 1.6 d 4. TBAF, THF	I (92) 91% ee	588
PhSiH ₃ (1.1 eq), (<i>S</i>)- 195 -2 <i>n</i> -BuLi (5 mol%), MeC ₆ H ₅ , 65°, 1 h	II (94) 10% ee	783
PhSiH ₃ (1.1 eq), (<i>R</i>)- 195 -2 <i>n</i> -BuLi (5 mol%), MeC ₆ H ₅ , 65°, 1 h	I (94) 10% ee	783
PMHS (1.1 eq), Et ₂ Zn (2 mol%), (<i>R,R</i>)-ebpe (20 mol%), vitride (3%), MeC ₆ H ₅ , rt, 24 h	I (—) 64% ee	594
MesPhSiH ₂ , [Rh(cod)Cl] ₂ (2.5 mol%), (-)- 34 , THF, rt	I (95) 98% ee	586
1. PhSiH ₃ (0.1 eq), 198 (2 mol%), MeOH, 60°, pyrrolidine, MeOH, THF 2. PMHS, ketone, MeOH (3-7 eq), 15°		587
		

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.												
<div>C₁₀</div> <div></div>	PMHS (4 eq), 124 (0.05 mol %) CuCl (1 mol %), NaOBu- <i>t</i> (1 mol %), MeC ₆ H ₅ , -50°, 4h	<div></div> (97) 90% ee	590												
<div>C₁₁</div> <div></div>	PhSiH ₃ (1.1 eq), (<i>S</i>)- 195 -2 <i>n</i> -BuLi (5 mol %), MeC ₆ H ₅ , 65°, 1 h	<div></div> 1 (9) 5% ee	783												
	PhSiH ₃ (1.1 eq), (<i>R</i>)- 195 -2 <i>n</i> -BuLi (5 mol %), MeC ₆ H ₅ , 65°, 1 h	<div></div> 10 (10) 5% ee	783												
	Ph ₂ SiH ₂ (1.25 eq), Rh[(NBD)Cl] ₂ (0.5%), ligand (0.5%), MeC ₆ H ₅	1 (—)	791												
	<table><tr><th>Ligand</th><th>Temp</th><th>% ee</th></tr><tr><td>116</td><td>-5°</td><td>84</td></tr><tr><td>117</td><td>-5°</td><td>86</td></tr><tr><td>119</td><td>0°</td><td>86</td></tr></table>	Ligand	Temp	% ee	116	-5°	84	117	-5°	86	119	0°	86		
Ligand	Temp	% ee													
116	-5°	84													
117	-5°	86													
119	0°	86													
<div></div>	1. 197 (4.5 eq), <i>n</i> -BuLi (9 eq), C ₆ H ₆ 2. PMHS (5 eq) 3. Add ketone, 2.5 d 4. TBAF, THF	<div></div> (96) 95% ee	588												
<div></div>	(3-FC ₆ H ₄) ₂ SiH ₂ (1.5 eq), [Rh(cod)]BF ₄ (1 mol %), 1 (1.1 mol %), THF, -40°, 24 h	<div></div> (90) 89% ee ^b	578												

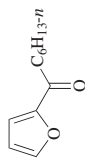


PMHS (1.2 eq), Et₂Zn (2 mol%), **131** (2 mol%),
MeC₆H₅, rt, 18 h

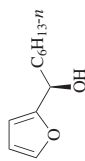


788

(0)

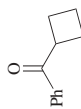


PMHS (4 eq), ligand (0.05 mol%), CuCl (x mol%),
NaOBu-*t* (y mol%), MeC₆H₅



590

Ligand	x	y	Temp	Time	% ee	
123	1	1	-50°	12 h	(98)	81
121	3	3	-78°	—	(—)	70
123	3	3	-50°	—	(—)	77



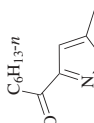
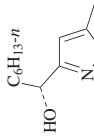
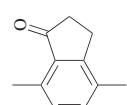
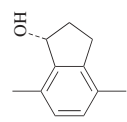
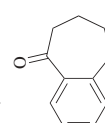
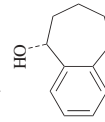

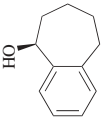

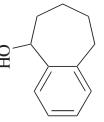
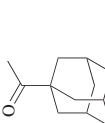
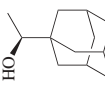

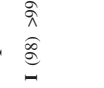
1. **197** (4.5 eq), *n*-BuLi (9 eq), C₆H₆
2. PhSiH₃ (1.5 eq)
3. Add ketone, 1 d
4. TBAF, THF



588

(88) 82% ee

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
<div>C₁₁</div> 	PMHS (4 eq), CuCl/NaOBu- <i>t</i> (1 mol%), 123 (0.05 mol%), MeC ₆ H ₅ , -50°, 10 h	 (68) 83% ee	590
	(MeO) ₃ SiH (1 eq), Li ₂ -histidine (10 mol%), THF/TMEDA, 0°, 24 h	 (66) 30% ee	593
	PMHS, Sn(OTf) ₂ (10 mol%), 87 (10 mol%), MeOH, rt	 (5) 33% ee	385
<div>C₁₁</div> 	Ph(1-Np)SiH ₂ (1.5 eq), [Rh(cod)]SbF ₆ (1 mol%), 126 (1 mol%), THF, -20°	 (90) 98% ee	576
<div>C₁₁</div> 	PhSiH ₃ (1.1 eq), (<i>R</i>) or (<i>S</i>)- 195-2<i>n</i> -BuLi (5 mol%), MeC ₆ H ₅ , 65°, 1 h	 (0)	783
<div>C₁₂</div> 	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1 mol%), DIOP (1.1 mol%), THF, rt, 48 h	 (92) 91% ee	606
<div>C₁₂</div> 	Ph(1-Np)SiH ₂ (1.5 eq), 126 (1 mol%), THF, -20°	 I (98) >99% ee	576

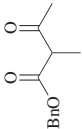
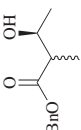
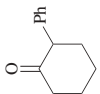
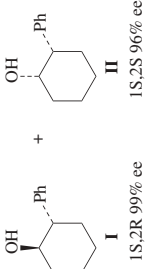
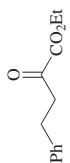
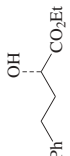
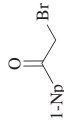
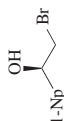


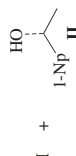




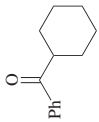

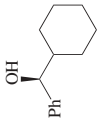
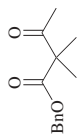
	Ph(1-Np)SiH ₂ (1.5 eq), [Rh(cod)]SbF ₆ (1 mol%), 126 (1 mol%), THF, -20°		(70) 70% ee	576																					
	Ph ₂ SiH ₂ (1.3 eq), RhCl ₃ (1 mol%), 87 (5 mol%), AgBF ₄ (2 mol%), THF, 0°, 1 d		I + II (92), I:II = 51:49 1S,2R 99% ee 1S,2S 96% ee	390																					
	PMHS, Sn(OTf) ₂ (10 mol%), 87 (10 mol%), MeOH, rt, 12-14 h		(98) 44% ee	385																					
	(EtO) ₃ SiH, THF, 198 , 96 h		(64) 84% ee R	794																					
	PMHS (1.1 eq), Et ₂ Zn (20 mol%), (S,S)-cbpe (20 mol%), vitride (3%), MeC ₆ H ₅ , rt, 24 h		(—) 75% ee	594																					
	PhSiH ₃ (1.1 eq), (S)- 195 -2 <i>n</i> -BuLi (5 mol%), MeC ₆ H ₅ , 65°, 3 h	I (94) 28% ee		783																					
	Ph ₂ SiH ₂ (1.2 eq), C ₆ H ₆ , catalyst (0.01 eq), 0-20°, 10-15 h			804																					
<table><tr><th>Catalyst</th><th>I + II</th><th>I:II</th></tr><tr><td>109</td><td>(82)</td><td>80.5:19.5</td></tr><tr><td>110</td><td>(60)</td><td>82.5:17.5</td></tr><tr><td>112</td><td>(56)</td><td>79:21</td></tr><tr><td>113</td><td>(84)</td><td>92:8</td></tr><tr><td>114</td><td>(95)</td><td>90:10</td></tr><tr><td>115</td><td>(92)</td><td>93.5:6.5</td></tr></table>					Catalyst	I + II	I:II	109	(82)	80.5:19.5	110	(60)	82.5:17.5	112	(56)	79:21	113	(84)	92:8	114	(95)	90:10	115	(92)	93.5:6.5
Catalyst	I + II	I:II																							
109	(82)	80.5:19.5																							
110	(60)	82.5:17.5																							
112	(56)	79:21																							
113	(84)	92:8																							
114	(95)	90:10																							
115	(92)	93.5:6.5																							

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂ 	Ph ₂ SiH ₂ (1.25 eq), Rh[(NBD)Cl] ₂ (0.5%), ligand (0.5%), MeC ₆ H ₅	 (—)	791
	Ligand Temp	% ee	
	116 0°	29	
	119 20°	42	
	109 20°	61	
	113 20°	84	
	PMHS (1.1 eq), Et ₂ Zn (20 mol%), (<i>R,R</i>)-ebpe (20 mol%), vitride (3%), MeC ₆ H ₅ , rt, 24 h	 (—) 80% ee	594
	1. 197 (4.5 eq), 2 <i>n</i> -BuLi, C ₆ H ₆		
	2. PMHS (5 eq)		
	3. Add ketone, 3 d	I (84) 95% ee	588
C ₁₃ 	PhSiH ₃ (1.1 eq), (<i>R</i>)- 195 -2 <i>n</i> -BuLi (5 mol%), C ₆ H ₅ Me, 65°, 1 h	I (100) 62% ee	783
	PhSiH ₃ (1.1 eq), (<i>S</i>)- 195 -2 <i>n</i> -BuLi (5 mol%), C ₆ H ₅ Me, 65°, 1 h	 (100) 25% ee	783
	1. 197 (4.5 eq), <i>n</i> -BuLi (9 eq), C ₆ H ₆		
	2. PhSiH ₃ (1.5 eq)		
	3. Add ketone, 2.5 d	 (88) 82% ee	588
	4. TBAF, THF		



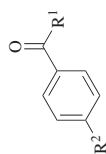
Ph(1-Np)SiH₂ (1.5 eq),
126 (1 mol%), THF, -20°

(80) >99% ee

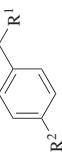


576

C₁₄:20



Cl₃SiH (1.5 eq), CHO (0.1 eq), CH₂Cl₂,
 0° to rt, 24 h



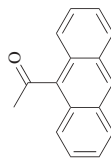
379

R ¹	R ²
4-ClC ₆ H ₄	Me
Ph	Et
BnCH ₂	Me
Ph	<i>i</i> -Bu
Ph	Bn

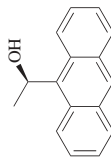
R ³
CONHPh
CONHPh
CONHNp-1
CONHNp-1
CONHNp-1

R,S
(87) 64:36
(47) 61:39
(76) 54:46
(21) 68:32
(27) 75:25

C₁₆



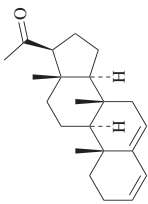
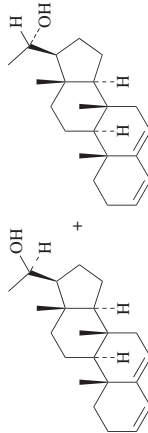
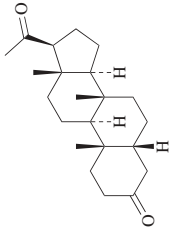
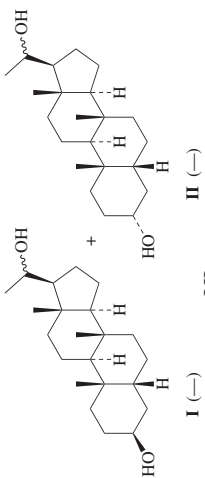
Ph₂SiH₂ (1.5 eq), [Rh(cod)Cl]₂ (0.25 mol%),
38 (0.5 mol%), Et₂O, rt



(100) 90% ee

571

TABLE 30. ASYMMETRIC ORGANOSILANE REDUCTION OF KETONES (Continued)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₂	Ph ₂ SiH ₂ , catalyst, C ₆ H ₆ , 22° Catalyst Rh-(+)-DIOP Rh-(-)-DIOP	 I:II 7:3 7:3	573
	Ph ₂ SiH ₂ , catalyst, C ₆ H ₆ , 22° Catalyst Rh-(+)-DIOP Rh-(-)-DIOP	 I:II 67:33 64:36	573

^a The catalyst is *S,S'*-1,2-bis(tetrahydroindeny)ethane/titanium (IV) and derivatives.^b The configuration of the product was not determined.^c The reducing agent was (EtO)₃SiH.^d 10 mol% of the catalyst was employed.^e 20 mol% of the catalyst was employed.^f An additional 5 mol% of BINOL was added.^g 10 mol% of cinchonidine was added.^h 1-Naphthylphenylsilane was used as the reducing silane.

TABLE 31. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES

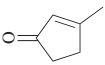
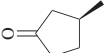
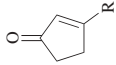
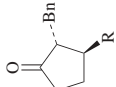
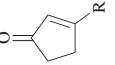
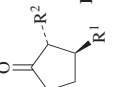
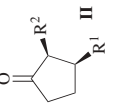




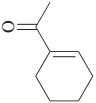


Enone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	PMHS (1.05 eq), CuCl (5 mol%), <i>t</i> -BuONa (5 mol%) (<i>S</i>)- <i>p</i> -Tol-BINAP (5 mol%), −78°, 24 h	 (42) 94% ee	595
C ₆₋₁₂ 	1. Ph ₃ SiH ₂ (0.53 eq), CuCl (5%), NaOBu- <i>t</i> (5%), (<i>S</i>)- <i>p</i> -Tol-BINAP, MeC ₆ H ₅ , 0°, 2–3 h 2. BnBr (x eq), TBAT (1.2 eq), temp		459
R	Solvent-2	x	Temp
Me	CH ₂ Cl ₂	2.0	rt
Me	THF	2.0	rt
Me	CH ₂ Cl ₂ /MeC ₆ H ₅	2.0	rt
BnCH ₂	CH ₂ Cl ₂	1.2	50°
BnCH ₂	CH ₂ Cl ₂ /MeC ₆ H ₅	1.4	rt
BnCH ₂	CH ₂ Cl ₂ /MeC ₆ H ₅	2.0	rt
BnCH ₂	CH ₂ Cl ₂ /MeC ₆ H ₅	3.0	rt
	1. Ph ₃ SiH ₂ (0.53 eq), CuCl (5%), NaOBu- <i>t</i> (5%), (<i>S</i>)- <i>p</i> -Tol-BINAP, MeC ₆ H ₅ , 0°, 2–3 h 2. R ² X, TBAT (1.2 eq), CH ₂ Cl ₂ /MeC ₆ H ₅ (1:1), rt, 24 h	 + 	459
R ¹	R ² X	I + II	I:II
Me	BnBr	(62)	92:8
Me	BrCH ₂ CO ₂ Et	(52)	94:6
Me	1-bromo-3-methyl-2-butene	(52)	80:20
BnCH ₂	<i>n</i> -Bul	(42)	85:15
BnCH ₂	BnBr	(67)	94:6
BnCH ₂	allyl bromide	(64)	76:24
BnCH ₂	MeI	(65)	73:27

TABLE 31. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Enone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	Ph ₂ SiH ₂ (1.5 eq), [Ir(cod)Cl] ₂ (0.25 mol%), (<i>R</i>)- 38 (0.5 mol%), Et ₂ O, 0°, 15 h	 (100) 84% ee ^a	582
C ₇ 	PMHS (1.05 eq), CuCl (5 mol%), <i>t</i> -BuONa (5 mol%), (<i>S</i>)-BIPHEMP (5 mol%), -78°, 24 h	 (61) 92% ee	595
C ₈ 	PMHS (2 eq), (Ph ₃ P)CuH (1 mol%), 124 (0.1-0.5 mol%), MeC ₆ H ₅ , 0°, 4.5 h	 (96) 90% ee	597
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1.0 mol%), 25 (1.1 mol%), -40°, THF, 4 h	 (71) 95% ee	577
	Ph(1-Np)SiH ₂ (1.5 eq), [Rh(cod)]SbF ₆ (1 mol%), 126 (1 mol%), THF, -20°	I (85) 91% ee	576
	1. 197 (4.5 eq), <i>n</i> -BuLi (9 eq), C ₆ H ₆ 2. PMHS (10 eq) 3. Add ketone. 3 d	I (70) 85% ee	588
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1 mol%), DIOP (1.1 mol%), THF, rt, 10 h	I (71) 95% ee	606

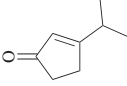
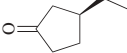
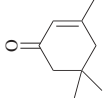
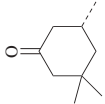
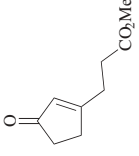
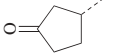
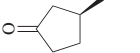
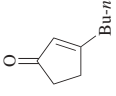
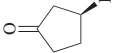
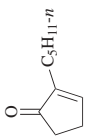
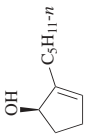
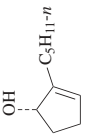
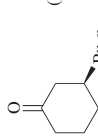
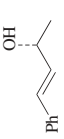
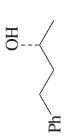
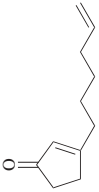
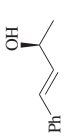
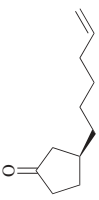
	PMHS (1.05 eq), CuCl (5 mol%), <i>i</i> -BuONa (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (5 mol%), 0°, 3 d		(88) 94% ee	595
	PMHS (2 eq), (Ph ₃ P)CuH (1 mol%), 124 (0.00036 mol%), MeC ₆ H ₅ , -35°, 3 d		(89) 98.5% ee	597
	PMHS (1 eq), (Ph ₃ P)CuH (1 mol%), 124 (0.1-0.5 mol%), 0°, 6 h	1 (>90)		597
	Solvent	% ee		
	CH ₂ Cl ₂	90		
	MeC ₆ H ₅	92		
	THF	95		
	dioxane/THF	98		
	PMHS (2 eq), (Ph ₃ P)CuH (1 mol%), 124 (0.1-0.5 mol%), MeC ₆ H ₅ , -78°, 18 h		(94) 97% ee	597
	PMHS (1.05 eq), CuCl (5 mol%), <i>i</i> -BuONa (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (5 mol%), 0°, 24 h		(86) 92% ee	595
	PMHS (1.05 eq), CuCl (5 mol%), <i>i</i> -BuONa (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (5 mol%), 0°, 12 h		(84) 98% ee	595

TABLE 31. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

Enone	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	1. PhSiH ₃ (0.1 eq), 198 (2 mol %), pyrrolidine, MeOH, THF, 60° 2. PMHS, ketone, MeOH (3-7 eq), 15°, 4 h	 (90) 84% ee	587
	Ph ₂ SiH ₂ (1.5 eq), [Rh(cod) ₂]BF ₄ (1.0 mol %), 25 (1.1 mol %), THF, -40°, 4 h	 (84) 87% ee	597
	PMHS (1.05 eq), CuCl (5 mol %), <i>t</i> -BuONa (5 mol %), (<i>S</i>)- <i>p</i> -Tol-BINAP (5 mol %), -78°, 2 d	 (82) 87% ee	595
	(MeO) ₃ SiH (1 eq), Et ₂ O/TMEDA (30:1), Li-(<i>R</i>)-BINOL (10 mol %), 0°, 24 h	 (91) 57% ee	592
	(MeO) ₃ SiH (1 eq), Li ₂ -histidine (10 mol %), THF/TMEDA, 0°, 24 h	 (91) 28% ee	593
C ₁₁ 	(MeO) ₃ SiH (1 eq), Li ₂ -histidine (10 mol %), THF/TMEDA, 0°, 24 h	 (78) 70% ee	593
	PMHS (1.05 eq), CuCl (5 mol %), <i>t</i> -BuONa (5 mol %), (<i>S</i>)-BINAP (5 mol %), 15°, 24 h	 (87) 96% ee	595

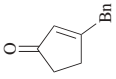
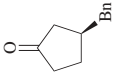
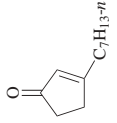
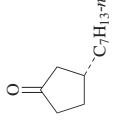
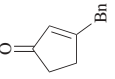
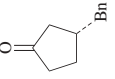
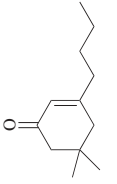
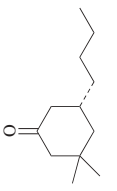
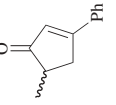
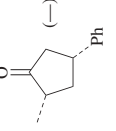
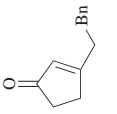
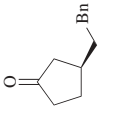
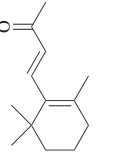
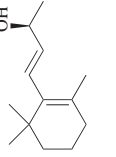
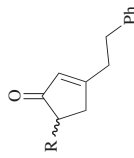
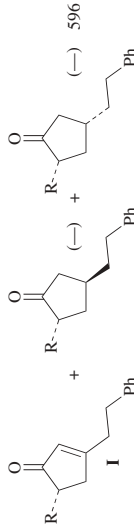
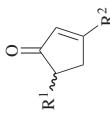
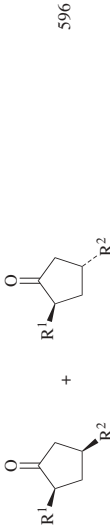
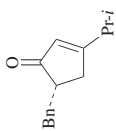
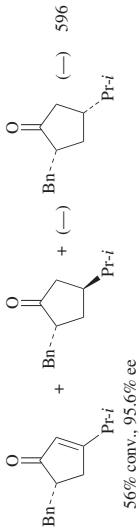
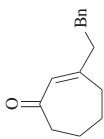
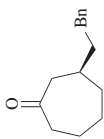
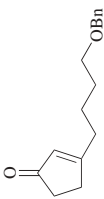

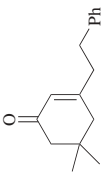
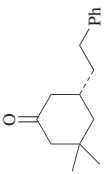
C ₁₂		PMHS (1.05 eq), CuCl (5 mol%), <i>t</i> -BuONa (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (5 mol%), 0°, 24 h		(78) 96% ee	595
		PMHS (2 eq), CuCl (1 mol%), NaOMe (0.5 mol%), 124 (0.4 mol%), MeC ₆ H ₅ , -78°		(97) 97.5% ee	597
		PMHS (2 eq), (Ph ₃ P)CuH (1 mol%), 124 (0.1-0.5 mol%), MeC ₆ H ₅ , -78°, 36 h		(92) 97.3% ee	597
		PMHS (2 eq), (Ph ₃ P)CuH (1 mol%), 124 (0.1-0.5 mol%), MeC ₆ H ₅ , 0°, 6 h		(90) 96% ee	597
C ₁₃		PMHS (1.1 eq), CuCl/NaOBu- <i>t</i> , (<i>S</i>)- <i>p</i> -Tol-BINAP (10 mol%), MeC ₆ H ₅ , then TBAF		45% conv., 71.6% ee	596
		PMHS (1.05 eq), CuCl (5 mol%), <i>t</i> -BuONa (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (5 mol%), 0°, 24 h		(86) 94% ee	595
		PMHS (1.1 eq), Et ₂ Zn (20 mol%), (<i>R,R</i>)-ebpe (20 mol%), vitride (3%), MeC ₆ H ₅ , rt, 24 h		(-) 18% ee	594

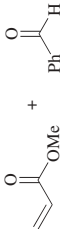
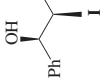
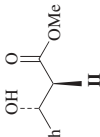

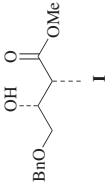
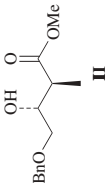
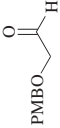
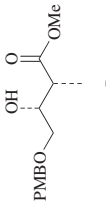
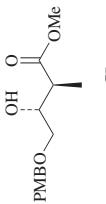
TABLE 31. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED KETONES (Continued)

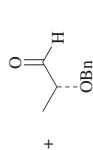
Enone	Conditions	Product(s) and Yield(s) (%)	Refs.	
	PMHS (1.1 eq), CuCl/NaOBu- <i>t</i> , (<i>S</i>)- <i>p</i> -Tol-BINAP (10 mol%), MeC ₆ H ₅ , temp; then TBAF		596	
R	Temp	% Conv. I	% ee	
Me	-78°	55.6	94.6	
<i>i</i> -Pr	0°	56.5	97.4	
<i>n</i> -Bu	-78°	53.2	90.6	
<i>t</i> -Bu	0°	50.7	91.0	
CH ₂ CO ₂ Bu- <i>t</i>	-50°	56.0	95.3	
	PMHS (2.2 eq), CuCl/(<i>S</i>)- <i>p</i> -Tol-BINAP (10 mol%), <i>t</i> -BuONa (1.7 eq), <i>t</i> -BuOH (5.0 eq), MeC ₆ H ₅ , temp, 26 h; then TBAF		596	
R ¹	R ²	I + II	I:II	% ee I
Me	BnCH ₂	(89)	91:9	91
<i>i</i> -Pr	BnCH ₂	(94)	93:7	93
<i>t</i> -Bu	BnCH ₂	(94)	93.5:6.5	94
<i>t</i> -BuO ₂ CCH ₂	BnCH ₂	(91)	90:10	93
Bn	<i>i</i> -Pr	(95)	91.5:8.5	93
Me	Ph	(90)	96.5:3.5	91

C ₁₅		PMHS (1.1 eq), CuCl/NaOBu- <i>t</i> , (<i>S</i>)- <i>p</i> -Tol-BINAP (10 mol%), MeC ₆ H ₅ ; then TBAF		596
C ₁₆		PMHS (1.05 eq), CuCl (5 mol%), <i>t</i> -BuONa (5 mol%), (<i>S</i>)-BINAP (5 mol%), -78°, 4 d	 (82) 96% ee	595
		PMHS (1.05 eq), CuCl (5 mol%), <i>t</i> -BuONa (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (5 mol%), 0°, 24 h	 (91) 94% ee	595
		PMHS (2 eq), (Ph ₃ P)CuH (1 mol%), 124 (0.1–0.5 mol%), MeC ₆ H ₅ , -35°, 16 h	 (95) 99.5% ee	597

^a The product is the (–) enantiomer.

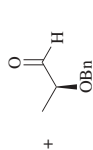
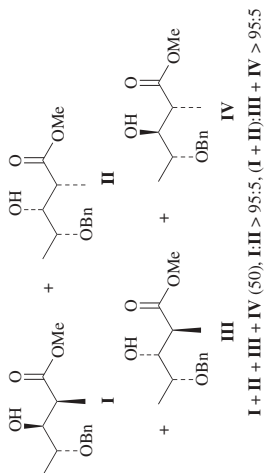
TABLE 32. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS

C ₄	Ester	Conditions	Product(s) and Yield(s) (%)		Refs.
		1. Et ₃ MeSiH, catalyst (5 mol%), ligand (7.5 mol%), CH ₂ Cl ₂ , rt, 24 h 2. H ₃ O ⁺			601
		Catalyst	Ligand		
		[Ir(cod)Cl] ₂	86		
		[Ir(cod)Cl] ₂	87		
		[Ir(cod)Cl] ₂	88		
		[Ir(cod)Cl] ₂	90		
		[Ir(cod)Cl] ₂	98		
		[Ir(coe) ₂ Cl] ₂	98		
		Ir(cod)BF ₄	98		
		(CO) ₂ Ir(acac)	98		
[Rh(cod)Cl] ₂	98				
		1. Et ₃ MeSiH, [Ir(cod)Cl] ₂ (2.5 mol%), 98 (7.5 mol %), rt, 24 h 2. H ₃ O ⁺			601, 602
		I + II (59), I:II = 9.5:1, er I = 98:2			
		1. Et ₃ MeSiH, [Ir(cod)Cl] ₂ (2.5 mol%), 98 (7.5 mol%), rt, 24 h 2. H ₃ O ⁺			602
		I + II (76), I:II = 6:1, er I > 95:5			



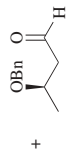
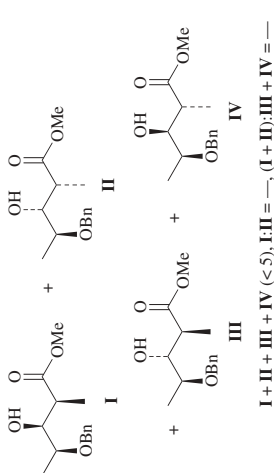
1. Et₃MeSiH, [Ir(cod)Cl]₂ (2.5 mol%),
98 (7.5 mol%), rt, 24 h
 2. H₃O⁺

601



1. Et₃MeSiH, [Ir(cod)Cl]₂ (2.5 mol%),
98 (7.5 mol%), rt, 24 h
 2. H₃O⁺

601



1. Et₃MeSiH, [Ir(cod)Cl]₂ (2.5 mol%),
98 (7.5 mol%), rt, 24 h
 2. H₃O⁺

601

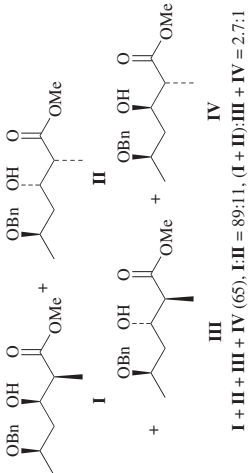


TABLE 32. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

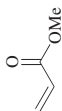
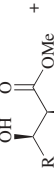
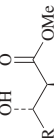





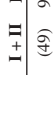


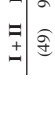

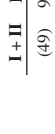

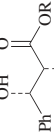


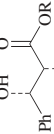

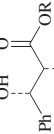
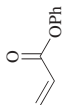
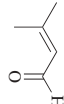
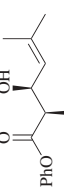
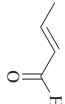
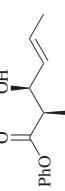
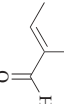
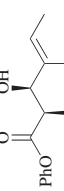
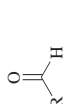
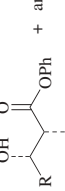
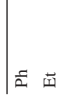
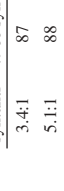
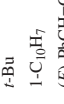
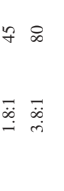
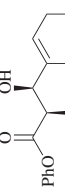
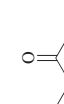
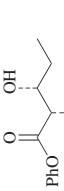




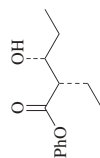
	Ester	Conditions	Product(s) and Yield(s) (%)				Refs.
C ₄		1. Et ₂ MeSiH, [Ir(cod) ₂ Cl] ₂ (2.5 mol%), 98 (7.5 mol%), CH ₂ Cl ₂ , rt, 24 h 2. H ₃ O ⁺		+		601	
							
							
C _{4,9}		1. Et ₂ MeSiH, [Rh(cod)Cl] ₂ (2.5 mol%), (R)-BINAP (6.5 mol%), CH ₂ Cl ₂ , rt, 24 h 2. H ₃ O ⁺		+		603	
							
							
C ₅		1. Et ₂ MeSiH, [Ir(cod) ₂ Cl] ₂ (5 mol%), 98 (7.5 mol%), CH ₂ Cl ₂ , rt, 45 h 2. H ₃ O ⁺		+		601	
							
							

TABLE 32. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Ester		Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉				(86) syn:anti = 6:1, 83% ee syn
	+	Et ₂ MeSiH (1.75 eq), {Rh(cod)}[(<i>R</i>)-BINAP]]BF ₄ (5 mol%), rt, 12 h		470
	+			(54) syn:anti = 6:1, 71% ee syn
	+	Et ₂ MeSiH (1.75 eq), {Rh(cod)}[(<i>R</i>)-BINAP]]BF ₄ (5 mol%), rt, 12 h		470
	+			(90) syn:anti = 3:1, 75% ee syn
C ₁₀	+	Et ₂ MeSiH (1.75 eq), {Rh(cod)}[(<i>R</i>)-BINAP]]BF ₄ (5 mol%), rt, 12 h		470
	+			603
	+	Et ₂ MeSiH (1.2 eq), [Rh(cod)Cl] ₂ (2.5 mol%), (<i>R</i>)-BINAP (6.5 mol%), CH ₂ Cl ₂ , rt, 24 h		
	+			
	+			
C ₁₀	+	Et ₂ MeSiH (1.75 eq), {Rh(cod)}[(<i>R</i>)-BINAP]]BF ₄ (5 mol%), rt, 12 h		(73) syn:anti = 7:1, 81% ee syn
	+			(76) syn:anti = 4.3:1, 88% ee syn
	+	Et ₂ MeSiH (5 eq), [Rh(cod)Cl] ₂ (5 mol%), (<i>S</i>)-BINAP (6.5 mol%), rt, 48 h		470
	+			
	+			

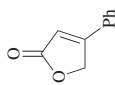


Et₂MeSiH (5 eq), [Rh(cod)Cl]₂ (5 mol%),
(S)-BINAP (6.5 mol%), rt, 48 h

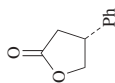


470

(52) syn:anti = 3.9:1, 88% ee syn

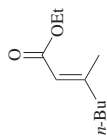


PMHS (2 eq), (Ph₃P)CuH (0.5 mol%),
124 (0.1 mol%), *t*-BuOH (1.1 eq), rt, 1 h

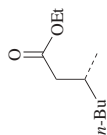


(96) 99% ee

598

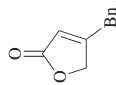


PMHS (2 eq), (Ph₃P)CuH (7.3 mol%),
124 (7.3 mol%), *t*-BuOH (1.13 eq),
MeC₆H₅, 0°

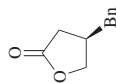


(80) 95% ee

598



Silane (4 eq), Cu salt (5 mol%),
NaOBu-*t* (5-20 mol%), additive,
(S)-*p*-Tol-BINAP (5 mol%)

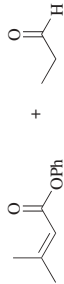

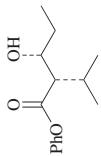
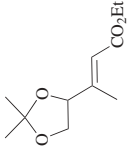
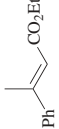
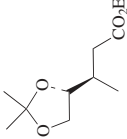
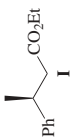


599

C₁₁

Silane	Cu Salt	Additive	Temp	Time	% ee
PMHS	CuCl	MeC ₆ H ₅	rt	48 h	(50) 80
Ph ₂ SiH ₂	CuCl	DEE/C ₅ H ₁₂	-15°	24 h	(34) 91
PMHS	CuCl	C ₆ H ₁₂ /EtOH	rt	5 min	(89) —
PMHS	CuCl	THF/C ₅ H ₁₂ /EtOH	-40°	4 h	(90) 93
PMHS	CuCl ₂ ·2H ₂ O	MeC ₆ H ₅ /C ₅ H ₁₂ / <i>i</i> -PrOH	-20°	3 h	(90) 92

TABLE 32. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}  + 	Et_3MeSiH (5 eq), $[Rh(cod)Cl]_2$ (5 mol %), (S) -BINAP (6.5 mol %), rt, 48 h	 (0)	470
C_{12}  	PMHS, CuH, 124 (0.2-0.4 mol %), <i>t</i> -BuOH, rt, 1 h	 (91) 98% ee	598
	PMHS (4 eq), $CuCl_2$ (0.1 mol %), $NaOBu-t$ (0.2 mol %), <i>t</i> -AmOH, (S) - <i>p</i> -Tol-BINAP (0.1 mol %), C_6H_{12} , rt	 (95) 86% ee	599
	PMHS (2 eq), $(Ph_3P)CuH$ (7.3 mol %), 124 (7.3 mol %), <i>t</i> -BuOH (1.13 eq), MeC_6H_5 , 0°	I (92) 98% ee	598
	PMHS (2 eq), $(Ph_3P)CuH$ (7.3 mol %), 124 (7.3 mol %), <i>t</i> -BuOH (1.13 eq), MeC_6H_5 , 0°	I (94) 91% ee	598
	PMHS (4 eq) $CuCl$ (5 mol %), $NaOBu-t$ (5 mol %), (S) - <i>p</i> -Tol-BINAP (10 mol %), MeC_6H_5 , rt, 24 h	I (84) 90% ee	600

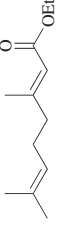

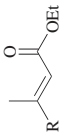
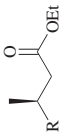
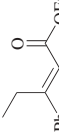
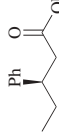
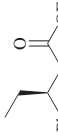
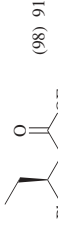

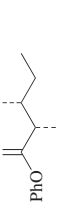

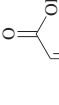
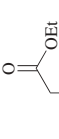

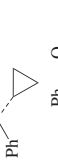
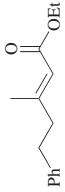
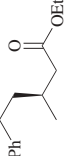
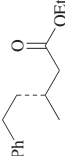
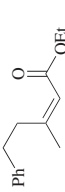
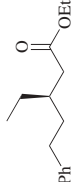
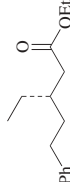
C ₁₃		PMHS (4 eq), CuCl (5 mol%), NaOBu- <i>t</i> (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (10 mol%), MeC ₆ H ₅ , rt, 25 h		600
		PMHS (4 eq), CuCl (5 mol%), NaOBu- <i>t</i> (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (10 mol%), MeC ₆ H ₅ , rt		600
C ₁₄		PMHS, CuH, 124 (0.2-0.4 mol%), <i>t</i> -BuOH, 0°, 1 h		598
		PMHS (4 eq), CuCl (5 mol%), NaOBu- <i>t</i> (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (10 mol%), MeC ₆ H ₅ , rt, 25 h		600
C ₁₄		Et ₃ MeSiH (5 eq), [Rh(cod)Cl] ₂ (5 mol%), (<i>S</i>)-BINAP (6.5 mol%), rt, 48 h		470
			(30) synanti = 4:4:1, — % ee syn	
C ₁₄		PMHS (2 eq), (Ph ₃ P)CuH (7.3 mol%), 124 (7.3 mol%), <i>t</i> -BuOH (1.13 eq), MeC ₆ H ₅ , 0°		598
		PMHS, CuH, 124 (0.2-0.4 mol%), <i>t</i> -BuOH, 0°, 1 h		598

TABLE 32. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED ESTERS (Continued)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	PMHS, CuH, 124 (0.2–0.4 mol%), <i>t</i> -BuOH, 0°, 1 h	 I (98) 99% ee	598
	PMHS (2 eq), (Ph ₃ P)CuH (7.3 mol%), 124 (7.3 mol%), <i>t</i> -BuOH (1.13 eq), MeC ₆ H ₅ , 0°	 II (98) 99% ee	598
	PMHS (2 eq), (Ph ₃ P)CuH (7.3 mol%), 124 (7.3 mol%), <i>t</i> -BuOH (1.13 eq), MeC ₆ H ₅ , 0°	II (98) 99% ee	598
	PMHS (4 eq), CuCl (5 mol%), NaOBu- <i>t</i> (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (10 mol%), MeC ₆ H ₅ , rt, 20 h	II (95) 84% ee	600
C_{15} 	PMHS (4 eq), CuCl (5 mol%), NaOBu- <i>t</i> (5 mol%), (<i>S</i>)- <i>p</i> -Tol-BINAP (10 mol%), MeC ₆ H ₅ , rt, 18 h	I (96) 83% ee	600
	PMHS, CuH, 124 (0.2–0.4 mol%), <i>t</i> -BuOH, rt, 1 h	 (93) 99% ee	598
	PMHS, CuH, 124 (0.2–0.4 mol%), <i>t</i> -BuOH, rt, 1 h	 (94) 98% ee	598

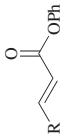

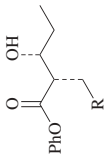
C ₁₅₋₁₈	 $\text{R}-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{OPh}$	+	 $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3$	Et ₃ MeSiH (5 eq), [Rh(cod)Cl] ₂ (5 mol%), (S)-BINAP (6.5 mol%), rt, 48 h	 $\text{PhO}-\text{C}(=\text{O})-\text{CH}(\text{OH})-\text{CH}_2-\text{R}$	470
R					syn:anti	% ee syn
<i>n</i> -C ₆ H ₁₃					(54) 4.2:1	88
TBSO(CH ₂) ₃					(53) 3.8:1	88
Ph(CH ₂) ₃					(49) 3.9:1	93

TABLE 33. ASYMMETRIC ORGANOSILANE REDUCTION OF α,β -UNSATURATED LACTAMS

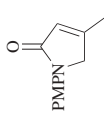
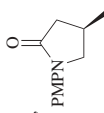
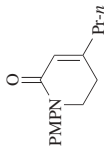
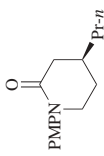
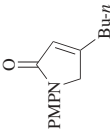
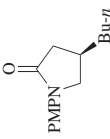
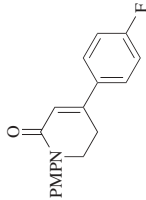
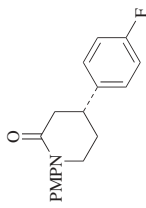
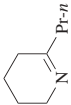
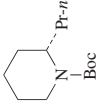
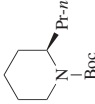


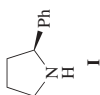
Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₂</p> 	<p>PMHS (4 eq), CuCl₂•2 H₂O (0.1 mol%), NaOBu-<i>t</i> (20 mol%), <i>t</i>-AmOH, (<i>S</i>)-<i>p</i>-Tol-BINAP (5 mol%), MeC₆H₅/C₅H₁₂, rt, 1 h</p>	<p>PMPN</p>  <p>(90) 92% ee</p>	599
<p>C₁₅</p> 	<p>PMHS (4 eq), CuCl₂•2 H₂O (5 mol%), NaOBu-<i>t</i> (20 mol%), <i>t</i>-AmOH, (<i>S</i>)-<i>p</i>-Tol-BINAP (20 mol%), MeC₆H₅/C₅H₁₂, 0°, 3 h</p>	<p>PMPN</p>  <p>(89) 91% ee</p>	599
<p>C₁₈</p> 	<p>PMHS (4 eq), CuCl₂•2 H₂O (5 mol%), NaOBu-<i>t</i> (20 mol%), <i>t</i>-AmOH, (<i>S</i>)-<i>p</i>-Tol-BINAP (20 mol%), MeC₆H₅/C₅H₁₂, 0°, 3 h</p>	<p>PMPN</p>  <p>(94) 94% ee</p>	599
	<p>PMHS (16 eq), CuCl₂•2 H₂O (2.5 mol%), NaOBu-<i>t</i> (5 mol%), <i>t</i>-AmOH (16 eq), (<i>R</i>)-<i>p</i>-Tol-BINAP (0.5 mol%), C₆H₅F, air, rt, 3 h</p>	<p>PMPN</p>  <p>(89) 90% ee</p>	599

TABLE 34. ASYMMETRIC ORGANOSILANE REDUCTION OF IMINES

Imine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ 	1. PhSiH ₃ (2 eq), <i>R,R</i> - 198 (1 mol%), pyrrolidine (0.1 eq), MeOH (0.1 eq), THF, rt, 6 h 2. (<i>trans</i> -BuO ₂ C) ₂ O	 (80) 99% ee	611
	1. PhSiH ₃ (2 eq), <i>S,S</i> - 198 (1 mol%), pyrrolidine (0.1 eq), MeOH (0.1 eq), THF, rt, 6 h 2. (<i>trans</i> -BuO ₂ C) ₂ O	 (82) 99% ee	611
C ₉ 	PhSiH ₃ (4 eq), 198 (1 mol%), rt, 12 h	 (100) 97% ee	612
	PMHS (10 eq), 198 (10 mol%), rt, 48 h	I (50) —% ee	612
	PhSiH ₃ (4.5 eq), 198 (1 mol%), rt, 12 h	I (94) 97% ee	610
	PhSiH ₃ (4.5 eq), 198 (0.02 mol%), 35°, 12 h	I (95) 99% ee	610
	Ph ₂ SiH ₂ (2 eq), 38 (10 mol%), [(Ph ₃ P)RuCl ₂] ₂ (10 mol%), MeC ₆ H ₅ , 0°, 90 h	I (51) 73% ee	605
	Ph ₂ SiH ₂ (2 eq), 38 (10 mol%), [Ir(cod)Cl] ₂ (10 mol%), Et ₂ O, 0°, 60 h	I (56) 89% ee	605
	Ph ₂ SiH ₂ (2 eq), 38 (10 mol%), [Ir(cod)Cl] ₂ (10 mol%), Et ₂ O, 0°, 48 h	I (24) 16% ee	605



Ph₂SiH₂ (2 eq), **38** (10 mol%),
metal complex (10 mol%),
MeC₆H₅, 0°



Metal Complex	Time	% ee
(Ph ₃ P)RuCl ₂	40 h	(60) 88
[Ir(cod)Cl] ₂	20 h	(>95) 85
[Rh(cod)Cl] ₂	20 h	(75) 34

Ph₂SiH₂ (2 eq),
metal complex (10 mol%),
ligand (5 mol%), Et₂O, 0°



Metal Complex	Ligand	Time	% ee
[Ir(cod)Cl] ₂	37	20 h	(>95) 85
[Ir(cod)Cl] ₂	37	60 h	(>95) 88
[Rh(cod)Cl] ₂	37	20 h	(75) 34
[Ir(cod)Cl] ₂	35	50 h	(78) 88
[Ir(cod)Cl] ₂	36	50 h	trace
[Ir(cod)Cl] ₂	38	30 h	(>95) 71
[Rh(cod)Cl] ₂	38	30 h	(17) 32
[Ir(cod)Cl] ₂	41	40 h	(>95) 86




















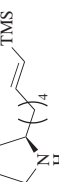
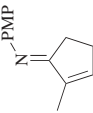

		613
PhSiH ₃ (1.1 eq), 198 , H ₂ (500 psig), 65°, 8 h	PhSiH ₃ (1.1 eq), 198 , H ₂ (500 psig), 65°, 8 h	
		612
PMHS (9 eq), 198 (0.5 mol%), <i>i</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	PMHS (9 eq), 198 (0.5 mol%), <i>i</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	
		612
PhSiH ₃ (9 eq), 198 (2 mol%), <i>s</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	PhSiH ₃ (9 eq), 198 (2 mol%), <i>s</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	
		612
PhSiH ₃ (9 eq), 198 (0.05 mol%), <i>i</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	PhSiH ₃ (9 eq), 198 (0.05 mol%), <i>i</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	
		607
Ph ₂ SiH ₂ (2 eq), [Rh(C ₂ H ₄) ₂] ₂ (2 mol%), (+)-DIOP, C ₆ H ₆ , 1°	Ph ₂ SiH ₂ (2 eq), [Rh(C ₂ H ₄) ₂] ₂ (2 mol%), (+)-DIOP, C ₆ H ₆ , 1°	
		613
PhSiH ₃ (2.5-3 eq), 198 , H ₂ (80 psig), 65°, 50 h	PhSiH ₃ (2.5-3 eq), 198 , H ₂ (80 psig), 65°, 50 h	
		613
PhSiH ₃ (2.5-3 eq), 198 , H ₂ (80 psig), 65°, 30 h	PhSiH ₃ (2.5-3 eq), 198 , H ₂ (80 psig), 65°, 30 h	
		613

TABLE 34. ASYMMETRIC ORGANOSILANE REDUCTION OF IMINES (Continued)

C ₁₂₋₁₈	Imine	Conditions	Product(s) and Yield(s) (%)		Refs.
		Cl ₃ SiH (1.5 eq), 162 (10 mol%), rt, 16 h		% ee	808
	R ¹	Solvent			
	Ph	CHCl ₃	(60)	<5	
	Ph	CH ₂ Cl ₂	(68)	79	
	Ph	CHCl ₃	(79)	86	
	Ph	MeCN	(65)	30	
	4-O ₂ NC ₆ H ₄	CHCl ₃	(30)	85	
	<i>c</i> -C ₆ H ₁₁	CHCl ₃	(80)	37	
	Ph	CHCl ₃	(50)	<5	
	4-MeOC ₆ H ₄	CHCl ₃	(62)	76	
	4-MeOC ₆ H ₄	CHCl ₃	(57)	80	
	Ph	CHCl ₃	(96)	85	
	Ph	CH ₂ Cl ₂	(36)	22	
	Ph	CHCl ₃	(46)	8	
	4-CF ₃ C ₆ H ₄	CHCl ₃	(43)	87	
	2-C ₁₀ H ₇	CH ₂ Cl ₂	(69)	80	
	2-C ₁₀ H ₇	CHCl ₃	(50)	87	
C ₁₃		PhSiH ₃ (2.5-3 eq), 198 , H ₂ (80 psig), 50°, 27 h		(73) 99% ee	613
		1. PMHS, 198 2. Add imine 3. <i>i</i> -BuNH ₂ , slow addition, 60°		(90) 98% ee	809

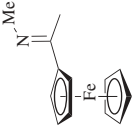
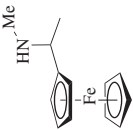

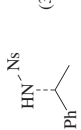

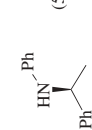


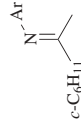
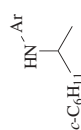
	<p>PhSiH₃ (4.5 eq), 198 (2.5 mol%), rt, 12 h</p>	 <p>(89) 86% ee (+)</p>	610
	<p>(MeO)₃SiH (2 eq), LiHMDS (40 mol%), BINOL (20 mol%), THF, additive (2 eq), -20°, 48 h</p>	 <p>(35) 72% ee</p>	608
	<p>Ph₃SiH₂ (2 eq), 37 (10 mol%), [Ir(cod)Cl]₂ (10 mol%), Et₂O, 0°, 60 h</p>	 <p>(51) 73% ee</p>	605
<p>1. PMHS, 198 2. Add imine 3. <i>i</i>-BuNH₂, slow addition, 60°</p>	<p>I (100) 13% ee</p>		809
	<p>PhSiH₃ (1.1 eq), 198, H₂ (80 psig), 65°, 10 h</p>	 <p>(82) 99% ee</p>	613
<p>1. PMHS, 198 2. Add imine 3. <i>i</i>-BuNH₂, slow addition, 60°</p>		 <p>(63) 99 (0) — (79) 99 (79) 99 (0) —</p>	809

TABLE 34. ASYMMETRIC ORGANOSILANE REDUCTION OF IMINES (Continued)

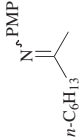
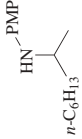

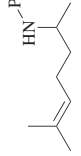


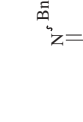
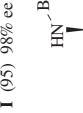
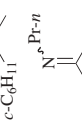
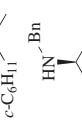
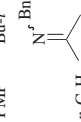
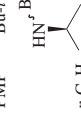
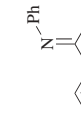
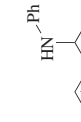
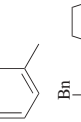
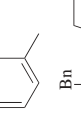
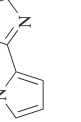
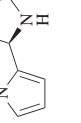
Imine	Conditions	Product(s) and Yield(s) (%)	Refs.																														
<div>C₁₄₋₁₅</div> <div></div>	<p>Ph₂SiH₂ (1.5 eq), [Rh(cod)Cl]₂ (2.5 mol %), 29 (5 mol %)</p> <table><tr><th>Solvent</th><th>Temp</th><th>Time</th></tr><tr><td>C₆H₆</td><td>rt</td><td>24 h</td></tr><tr><td>Et₂O</td><td>0°</td><td>140 h</td></tr><tr><td>THF</td><td>0°</td><td>140 h</td></tr><tr><td>Et₂O</td><td>0°</td><td>45 h</td></tr><tr><td>THF</td><td>0°</td><td>45 h</td></tr></table>	Solvent	Temp	Time	C ₆ H ₆	rt	24 h	Et ₂ O	0°	140 h	THF	0°	140 h	Et ₂ O	0°	45 h	THF	0°	45 h	<div></div> <table><tr><th></th><th>% ee</th></tr><tr><td>(54)</td><td>0</td></tr><tr><td>(28)</td><td>53</td></tr><tr><td>(37)</td><td>18</td></tr><tr><td>(52)</td><td>11</td></tr><tr><td>(47)</td><td>7</td></tr></table>		% ee	(54)	0	(28)	53	(37)	18	(52)	11	(47)	7	789
Solvent	Temp	Time																															
C ₆ H ₆	rt	24 h																															
Et ₂ O	0°	140 h																															
THF	0°	140 h																															
Et ₂ O	0°	45 h																															
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(52)	11																																
(47)	7																																
<div>C₁₄₋₁₆</div> <div></div>	<p>Ph₂SiH₂ (2 eq), [Rh(C₂H₄)₂]₂ (2 mol %), (+)-DIOP, C₆H₆</p>	<div></div> <table><tr><th>Temp</th><th>% ee</th></tr><tr><td>5°</td><td>(90) 47</td></tr><tr><td>24°</td><td>(98) 50</td></tr><tr><td>2°</td><td>(97) 65</td></tr><tr><td>24°</td><td>(40) 11.5</td></tr></table>	Temp	% ee	5°	(90) 47	24°	(98) 50	2°	(97) 65	24°	(40) 11.5	607																				
Temp	% ee																																
5°	(90) 47																																
24°	(98) 50																																
2°	(97) 65																																
24°	(40) 11.5																																
<div>C₁₄₋₁₈</div> <div></div>	<p>Cl₃SiH (1.5 eq), (<i>S</i>)-phenyl-<i>N</i>-formylprolinamide (0.1–0.2 eq), CH₂Cl₂, rt, 24 h</p>	<div></div> <table><tr><th></th><th>% ee</th><th>Conf.</th></tr><tr><td>(91)</td><td>55</td><td>R</td></tr><tr><td>(>99)</td><td>49</td><td>—</td></tr><tr><td>(95)</td><td>54</td><td>—</td></tr><tr><td>(97)</td><td>55</td><td>R</td></tr><tr><td>(56)</td><td>49</td><td>—</td></tr></table>		% ee	Conf.	(91)	55	R	(>99)	49	—	(95)	54	—	(97)	55	R	(56)	49	—	609												
	% ee	Conf.																															
(91)	55	R																															
(>99)	49	—																															
(95)	54	—																															
(97)	55	R																															
(56)	49	—																															



Cl₃SiH (1.5 eq),
catalyst (10 mol%), rt, 16 h

R ¹	R ²	Catalyst	Solvent	% ee
Ph	Ph	162	CHCl ₃	(49) 92
<i>c</i> -C ₆ H ₁₁	Ph	162	CHCl ₃	(53) 59
Ph	Ph	163	CH ₂ Cl ₂	(62) 70
Ph	Ph	163	CHCl ₃	(62) 85
2-C ₁₀ H ₇	Ph	163	CH ₂ Cl ₂	(53) 66
Ph	Ph	164	CHCl ₃	(81) 82
4-CF ₃ C ₆ H ₄	Ph	164	CHCl ₃	(94) 77
Ph	4-MeOC ₆ H ₄	164	CHCl ₃	(82) 79
Ph	Ph	165	CHCl ₃	(94) 92
4-MeOC ₆ H ₄	Ph	165	CHCl ₃	(62) 87
4-CF ₃ C ₆ H ₄	Ph ^c	165	CHCl ₃	(95) 89
Ph	4-MeOC ₆ H ₄	165	CHCl ₃	(85) 90
4-MeOC ₆ H ₄	Ph	165	MeC ₆ H ₅	(86) 85
4-CF ₃ C ₆ H ₄	Ph	165	MeC ₆ H ₅	(86) 89
Ph	4-MeOC ₆ H ₄	165	MeC ₆ H ₅	(85) 91
2-MeC ₆ H ₄	Ph	165	MeC ₆ H ₅	(90) 92
Ph	Ph	166	CHCl ₃	(88) 53
4-CF ₃ C ₆ H ₄	Ph	166	CHCl ₃	(92) 69
Ph	Ph	167	CHCl ₃	(35) 56
Ph	Ph	168	CHCl ₃	(0) —
Ph	Ph	169	CHCl ₃	(23) 7

TABLE 34. ASYMMETRIC ORGANOSILANE REDUCTION OF IMINES (Continued)

Imine	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅			
 $n\text{-C}_6\text{H}_{13}\text{-CH=N-CH(CH}_3)_2$ (PMP)	1. PMHS, 198 2. Add imine 3. <i>i</i> -BuNH ₂ , slow addition, 60°	 $n\text{-C}_6\text{H}_{13}\text{-CH}_2\text{-CH}_2\text{-CH(CH}_3)_2$ (70) 88% ee ^b	809
 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (PMP)	1. PMHS, 198 2. Add imine 3. <i>i</i> -BuNH ₂ , slow addition, 60°	 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (68) 90% ee ^b	809
 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (PMP)	PhSiH ₃ (10 eq), 198 (10 mol%), rt, 96 h	 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (55) 47% ee	612
 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (PMP)	PMHS (9 eq), 198 (0.5 mol%), <i>i</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ I (95) 98% ee	612
 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (PMP)	PMHS (9 eq), 198 (0.5 mol%), <i>i</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (96) 91% ee	612
 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (PMP)	PhSiH ₃ (9 eq), 198 (0.5 mol%), <i>i</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (90) 97% ee	612
 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (PMP)	PMHS (9 eq), 198 (1 mol%), <i>i</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (96) 69% ee	612
 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (PMP)	1. PMHS, (EBTH)TiF ₂ 2. Add imine 3. <i>i</i> -BuNH ₂ , slow addition, 60°	 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (28) 9% ee ^b	809
 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (PMP)	PhSiH ₃ (2.5-3 eq), 198 , H ₂ (80 psig), rt, 24 h	 $(E)\text{-3-methylpent-2-en-1-ylidene-N-methyl-N-(2-methylbut-3-en-1-yl)carbamate}$ (79) 95% ee	613



608



(MeO)₃SiH (2 eq), *n*-BuLi (40 mol%),
catalyst (20 mol%), THF, rt, 48 h

Catalyst	% ee	Conf.
(<i>S</i>)-isoleucinol	(56) 13	S
(<i>S</i>)-valinol	(28) 13	S
(<i>S</i>)-phenylalaninol	(45) 4	S
(<i>S</i>)-proline	(48) 1	S
(<i>R,R</i>)-2,3-butanediol	(60) 28	R
(<i>R,R</i>)-hydrobenzoin	(37) 32	R
TADDOL	(68) 2	R
(<i>R</i>)-BINOL	(53) 57	R
221	(37) 21	R
222	(27) 2	R
(<i>R</i>)-1-phenylethanol	(49) 0	—

(MeO)₃SiH (2 eq), base (40 mol%),
221 (20 mol%), THF, additive (2 eq),
rt, 48 h

I

608

Base	Solvent	Additive	Temp	% ee	Conf.
<i>n</i> -BuLi	THF	none	rt	(53) 57	R
LiHMDS	THF	none	rt	(38) 54	R
NaHMDS	THF	none	rt	trace	—
KHMDS	THF	none	rt	trace	—
<i>n</i> -BuLi	THF	TMEDA	rt	(52) 51	R
<i>n</i> -BuLi	THF	none	0°	(43) 65	R
<i>n</i> -BuLi	Et ₂ O	none	rt	(30) 12	S
LiHMDS	Et ₂ O	none	rt	(65) 31	S
<i>n</i> -BuLi	Et ₂ O	TMEDA	rt	(63) 59	R
<i>n</i> -BuLi	(<i>i</i> -Pr) ₂ O	none	rt	(28) 6	S
<i>n</i> -BuLi	MeC ₆ H ₅	none	rt	(4) 11	S

TABLE 34. ASYMMETRIC ORGANOSILANE REDUCTION OF IMINES (Continued)

Imine	Conditions	Product(s) and Yield(s) (%)	Refs.																												
C₁₆₋₁₉ 	PhSiH ₃ (9 eq), 198 , (0.5 mol%), <i>i</i> -BuNH ₂ (1.5 eq), 65°, 2.5 h	 Ar R 4-ClC ₆ H ₄ Me Ph <i>i</i> -Bu	612																												
	PMHS (10 eq), 198 , (1 mol%), amine, rt	 HN—Bn	612																												
	<table border="1"> <thead> <tr> <th>Amine</th><th>Time</th><th>% ee</th><th>% Conv.</th></tr> </thead> <tbody> <tr> <td>none</td><td>24 h</td><td>—</td><td>5</td></tr> <tr> <td><i>n</i>-C₆H₁₃NH₂</td><td>2 h</td><td>85</td><td>100</td></tr> <tr> <td><i>t</i>-BuNH₂</td><td>24 h</td><td>—</td><td>39</td></tr> <tr> <td>pyrrolidine</td><td>24 h</td><td>—</td><td>4</td></tr> <tr> <td><i>i</i>-BuNH₂</td><td>2 h</td><td>92</td><td>100</td></tr> <tr> <td><i>s</i>-BuNH₂</td><td>2 h</td><td>78</td><td>75</td></tr> </tbody> </table>	Amine	Time	% ee	% Conv.	none	24 h	—	5	<i>n</i> -C ₆ H ₁₃ NH ₂	2 h	85	100	<i>t</i> -BuNH ₂	24 h	—	39	pyrrolidine	24 h	—	4	<i>i</i> -BuNH ₂	2 h	92	100	<i>s</i> -BuNH ₂	2 h	78	75		
Amine	Time	% ee	% Conv.																												
none	24 h	—	5																												
<i>n</i> -C ₆ H ₁₃ NH ₂	2 h	85	100																												
<i>t</i> -BuNH ₂	24 h	—	39																												
pyrrolidine	24 h	—	4																												
<i>i</i> -BuNH ₂	2 h	92	100																												
<i>s</i> -BuNH ₂	2 h	78	75																												
C₁₈ 	1. PMHS, 198 2. Add imine 3. <i>t</i> -BuNH ₂ , slow addition, 60° Ph ₂ SiH ₂ (2 eq), [Rh(C ₂ H ₄) ₂] ₂ (2 mol%), (+)-DIOP, C ₆ H ₆ , 1°	 HN—PMP (90) 19% ee ^b Bn (78) 22.5% ee	809 607																												
	1. PMHS, 198 2. Add imine 3. <i>t</i> -BuNH ₂ , slow addition, 60°	 HN—PMP (25) 6% ee ^b	809																												

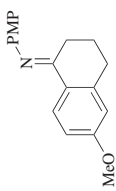
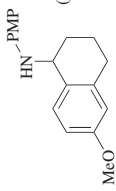
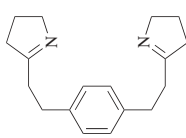
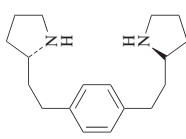
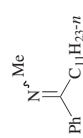
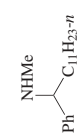
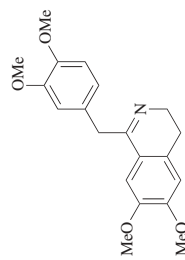
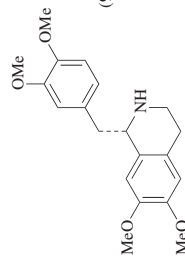
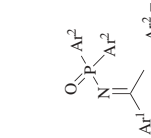
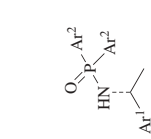
	<p>1. PMHS, 198 2. Add imine 3. <i>i</i>-BuNH₂, slow addition, 60°</p>	 <p>(63) 75% ee^b</p>	809
	<p>PhSiH₃ (4.5 eq), 198 (2 mol%), rt, 12 h</p>	 <p>(64) 98% ee</p>	610
	<p>PhSiH₃ (4.5 eq), 198 (2.5 mol %), 50°, 12 h</p>	 <p>(88) 9% ee</p>	610
	<p>Ph₂SiH₂ (2 eq), [Rh(C₂H₄)₂]₂ (2 mol %), (+) -DIOP, C₆H₆, 1°</p>	 <p>(98) 38.7% ee</p>	607
	<p>(HMe₂Si)₂O (3 eq), CuCl (1 mol %), NaOMe (1 mol %), 124 (1 mol %), <i>t</i>-BuOH (3 eq), MeC₆H₅, rt, 17 h</p>	 <p>(95) 95.3 (87) 93.5</p>	614

TABLE 34. ASYMMETRIC ORGANOSILANE REDUCTION OF IMINES (Continued)

Imine	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24+26} <div> </div>	(HMe ₂ Si) ₂ O (3 eq), CuCl (6 mol%), NaOMe (6 mol%), 124 (6 mol%), <i>t</i> -BuOH (3.3 eq), MeC ₆ H ₅ , rt, 17 h	<div> </div> % ee (94) 99.3 (96) 97.5 (93) 97.3 (95) 96.1 (98) 94.2 (94) 97.3	614
C_{25} <div> </div>	(HMe ₂ Si) ₂ O (3 eq), CuCl (6 mol%), NaOMe (6 mol%), 124 (6 mol%), <i>t</i> -BuOH (3.3 eq), MeC ₆ H ₅ , rt, 17 h	<div> </div> (93) 98.4% ee	614
C_{26} <div> </div>	(HMe ₂ Si) ₂ O (3 eq), CuCl (6 mol%), NaOMe (6 mol%), 124 (6 mol%), <i>t</i> -BuOH (3.3 eq), MeC ₆ H ₅ , rt, 17 h	<div> </div> (93) 97.6% ee	614

^a (+)-DIOP was used as the ligand.^b The configuration of the product was not determined.^c This reaction was carried out at -20°.

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